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Pittsburgh 13, Pennsylvania

MOBILITIES IN DIFFUSION IN ALPHA BRASS

By

G. T. Horne and R. E. Mehl



TECHNICAL REPORT

OFFICE OF NAVAL RESEARCH

Contract N6ori-47/IV - Project NR 031-134

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Office of Naval Research

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G. T. Horne and R. F. Mehl

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MOBILITIES IN DIFFUSION IN ALPHA BRASS

G. T. Horne* and R. F. Mehl*

ABSTRACT

Diffusion coefficients and mobilities were determined as functions of concentration in the alpha phase of the copper-zinc system. Use was made of incremental diffusion couples to determine the Kirkendall effect at various concentrations; Darken's analysis was used to calculate the individual diffusion coefficients and mobilities from these data.

The general diffusion coefficient is a single-valued function of the concentration in this system to within the limits of accuracy of the experimental methods used.

The form of the various functions (diffusion coefficients and mobilities) of concentration is the same in every case: it is essentially the same as the usual D vs c curve.

INTRODUCTION

As Darken¹ has pointed out, the knowledge that the movements of different atoms diffusing in the same lattice need not proceed at the same rate is old. Ionic lattices are the classical examples; the generalization to lattices with metallic

* G. T. Horne, Junior Member AIME, is Assistant Professor and R. F. Mehl, Member AIME, is Professor, Department of Metallurgical Engineering, Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

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bonding was slower in gaining acceptance. It remained for Kirkendall^{2,3,4} to show clearly that metallic diffusion need not be symmetrical with respect to both species. Several investigators⁵⁻⁸ have confirmed the initial observation of a "Kirkendall effect," that is, marker movement accompanying diffusion, and extended it to other systems and conditions. The theoretical interpretations have been many⁹; one of the first and simplest of these is that of Darken¹⁰ which is essentially mechanism independent. Darken has shown that the Kirkendall experiment permits a calculation of the individual diffusion coefficients, and, coupled with activity data, offers a means of measuring the mobilities of the separate atoms in a binary diffusion process.

There is no published information on the effects of concentration and temperature on the individual diffusion coefficients or on the mobility values in binary solid solution; this paper provides such information for zinc and copper in alpha brass.

For purposes of clarity, we shall designate the overall D value obtained, for example, from the Boltzmann-Matano solution to Fick's Law, as the "general diffusion coefficient;" and we shall designate the diffusion coefficients for the separate diffusing species as the "individual diffusion coefficients."

EXPERIMENTAL PROCEDURE

The authors have accepted Darken's¹⁰ analysis and have measured mobilities on this basis. The findings of da Silva

and Mehl⁵ are accepted: that the Matano interface, defined as the origin of coordinates for the Boltzmann-Matano solution to Fick's Law, coincides with the original weld interface; that the 'shift' of a marker is the distance between the Matano interface and the marker; that the observed porosity is too small sensibly to affect this result; and that the shift is a linear function of the Matano area, - the area defined as the absolute magnitude of the area on either side of the Matano interface.

Alloys

The alpha-phase of the copper-zinc system was chosen for investigation. There were many reasons for this choice: the phase is wide in concentration range, allowing for less percentage error in analytical determinations; the Kirkendall effect is large, promising better determinations of the velocity of the marker necessary in calculations; good activity measurements are available for the system; although da Silva and Mehl studied some six alloy systems, the results of pertinence here (see above) were deduced almost entirely on the Cu-Zn system but, conceivably, might not be valid in others.

The measurements were made on incremental couples, for two separate reasons: it has been questioned whether D , the general diffusion coefficient, is a single-valued function of concentration - a comparison of the D -values for couples with small concentration range, e.g., 10 vs 20 per cent Zn, against those from a wide concentration range, e.g.,

0 vs 30 per cent Zn, will answer that question; on the Darken analysis, the mobility can be determined only at the concentration at which the marker is observed to lie - this is but one concentration in a single couple - but choosing a series of incremental couples in the range between 0 and 30 per cent Zn provides mobility values at several concentrations, thus giving mobility as a function of concentration. Four alloys were chosen; nominally, pure copper, copper with 10% zinc, copper with 20% zinc, and copper with 30% zinc. This allowed six different types of diffusion couples to be prepared, promising mobility determinations at six different concentrations, but having a minimum range of 10% zinc. The copper was a specially prepared pure copper supplied through the courtesy of the American Smelting and Refining Company; the 30% zinc alloy was a special naval cartridge brass, supplied by the Naval Gun Factory; the 10% zinc and the 20% zinc alloys were selected commercial alloys supplied by the American Brass Company; analyses, obtained from the supplier, are to be found in Table 1. Analyses of the brasses, done in concurrence with the analytical work on the diffusion couples, agreed with those supplied.

The brasses were received in the form of rolled and annealed plate approximately one-half inch thick. Grain size determinations, longitudinal and transverse (both across the plate and through its thickness) showed an equiaxed structure; these determinations are shown in Table 1a. The copper was received as as-cast one-inch diameter rods; the grain size (also shown in Table 1a) was very large. The grain size after diffusion was large; the average grain diameter was 5-10 mm, being

Table 1
Analyses of Alloys Used in This Investigation

Alloy (Nominal)	Cu	Zn	Pb	Fe	Constituent Sn Sb (in weight percent)	Ni	Bi	As	Te	C	Cu Atomic %	Zn
Cu			0.0001	0.0001	nil	0.0001	0.0003	0.00001	0.0005	0.0001 Saturated	100	0
Cu - 10Zn	90.18	9.80*	0.005	0.01							90.4	9.6
Cu - 20Zn	80.20	19.78*	0.005	0.01							80.6	19.4
Cu - 30Zn	70.04	29.96*	0.02	0.05	0.02						70.6	29.4

* Zinc analyses by difference only.

Table 1a
Alloy (Nominal) Average Grain Diameter in Millimeters Grain Size

Cu	~10
Cu - 10Zn	0.065
Cu - 20Zn	0.065
Cu - 30Zn	0.090

larger for couples showing greater diffusion - higher temperature and/or longer time and/or greater gradient. (The grain length, in the direction of diffusion, was not so great; it was limited to the zone of diffusion.)

From the brass plates, discs approximately 1-1/4 inch in diameter were cut; the copper rods were cut into discs approximately 3/8 inch thick. The discs were turned down slightly and were accurately faced flat on both sides - the flats were perpendicular to the turned cylindrical surface and parallel to each other. The discs were then given a metallographic polish and cleaned.

The markers used were 3 mil tungsten wire supplied by the Sylvania Electric Products Company. As was mentioned by da Silva and Mehl⁵, this is about the smallest size wire that can be conveniently distinguished during the machining of the diffused couple. The wire was wound around one of the discs of the prospective diffusion couple (in the case of the triple-disc couples, the one chosen was, of course, the center disc) to give four or five strands marking the interface. The couple was then assembled and pressed to approximately 5000 lbs. to embed the wires in the alloys.

All diffusion couples studied in this work were pressure-welded from discs of the alloys described above. Consideration was given to preparation of couples by electroplating; in view of the apparent precision in the direct measurements of the distance between wire interfaces in the Smigelskas and Kirkendall experiment using electroplated copper and of the large scatter in similar measurements of da Silva and Mehl on pressure-welded couples, the welding of couples would appear to

introduced distortions and concurrent uncertainties. And brasses can be plated, but the operation was felt to be unsuited to the build-up of a relatively thick layer of homogeneous brass.

It was originally intended to make all diffusion couples in duplicate: one for chemical analysis, using 3 mil wires, and one for direct measurement of shift, using 0.5 mil wire. It was found, as it was by da Silva and Mehl, that, despite all possible precautions in preparation of welded couples, the direct measurement of shift was subject to so great a scatter as to render the data meaningless. This practice was discontinued.

Pressed couples were placed in a vertical furnace of da Silva's design⁵ and welded, under pressure, at a nominal temperature of 50°C below the solidus of the lower-melting alloy. They were held at temperature for one-half hour. Heating times ran in the neighborhood of one-half hour; cooling times were somewhat longer. Welding was done in an atmosphere of flowing dried hydrogen. The temperatures at which welding was done are not accurately known; they were measured by thermocouple, but the thermocouples were not calibrated and thermal gradients around the diffusion couples were not investigated. The amount of diffusion that occurred during welding was considered to be small with respect to that during the diffusion run and was neglected. That this was a reasonable assumption is shown by the fact that duplicate diffusion runs, at short and long times (see below), yielded the same diffusion-penetration curves when plotted on a reduced coordinate of x/\sqrt{t} .

Diffusion Treatments

The diffusion of the welded couples was carried out in bombs of 1-1/2" I.D. black iron pipe, closed on both ends with standard caps. The couples were placed in the bombs "floating" in a mixture of lampblack and chips of brass of the zinc content of the highest brass in any of the couples in that bomb. The machined chips served as a reservoir of zinc vapor to protect the couples from dezincification; the lampblack kept the couples away from each other, the chips and the interior of the bomb.

The diffusion runs were carried out in a flowing hydrogen and/or nitrogen atmosphere in two resistance wound furnaces built around 48" x 2-1/4" I.D. McDanel tubes. The furnaces, as constructed, had a constant temperature zone of 8 linear inches; in this zone, determined at 850°C in an empty furnace but with a flowing atmosphere, the temperature did not vary with position or time more than 2°C over a two-hour period. Outside of this region, the temperature, determined in the same manner, dropped more and more steeply toward the ends of the furnace; two more inches saw a temperature drop of 10°C.

A maximum of six diffusion couples, three in each of two bombs, were run at the same time. This assembly covered a maximum of 12-1/2 inches; no determination of temperature gradient was attempted in a loaded furnace - the bombs very nearly filled the cross-section of the furnace. The temperature of the run was measured at the end of the bomb and this was considered representative of all couples present. In view of the good temperature characteristics of the empty furnace and the good conductivity of both bombs and couples, this appears to

be a good assumption.

The furnaces were controlled by a Celectray controller activated by thermocouples embedded in the furnace windings; the temperature of the run was measured by thermocouples placed in the ends of the furnaces up against the bombs. The temperature was measured usually every half hour during the daytime and during at least one continuous 24-hour period for each separate run. The thermocouples used were of chromel-alumel and were given secondary calibration against a Bureau of Standards Pt-Pt, Rh thermocouple. As a check against progressive deterioration of these couples, temperature were checked at least three times each twenty-four hours with a calibrated Pt - Pt, 10 Rh thermocouple. No deterioration was observed except in one case; here, mishandling was probably the cause.

The long-time characteristics of the controller-furnace arrangement showed a random migration of some 3°C total range. An integration of the time-temperature record (including heating and cooling times) was made by inspection; it is felt that the values reported are within $\pm 2^{\circ}\text{C}$ and 1/2 hour elapsed time in all cases except Run 10; here the time may perhaps be in error by 1 hour.

Two temperatures were selected to be the primary basis for this work - ca. 780°C and 850°C; runs also were made at two temperatures above these and at one below. Triple disc couples (double diffusion couples) were used for long-time runs at the base temperatures and duplicate short-time runs were also made in an effort to check the data at these base temperatures.

In addition, duplicates of these runs were made to allow for the possibility that couples might part during machinings. Full data on all couples, and the diffusion runs, can be found in Table 2.

Machining

After the diffusion anneal, two parallel flat surfaces, approximately one-half inch wide, were carefully machined parallel to the cylindrical axis of the couple. These surfaces were so oriented as to be as nearly as possible normal to the axes of the wire markers. The surfaces were given a metallographic polish and were etched so that the wires were easily visible under low power magnification.

The couple was mounted in a lathe and, with the aid of a low power telescope and the wire ends, the wire interface was aligned perpendicular to the lathe axis. The specimen was now turned to a diameter of 0.6-0.8 inch depending upon the original size of the couple (the copper discs were originally < 1.00 inch in diameter; the brasses, ca. 1.25 inches), the length of the diffusion run and the ambient vapor pressure of zinc during the run. The end of the couple was then machined away and the cutting of specimens for analysis begun at a distance from the interface approximately 50% larger than the distance at which the first detectable concentration difference was to be expected.

In the region where the concentration-penetration curve was expected to be flat, samples of 8-mil thickness were cut; as the interface was approached this was lowered to 4, then 2 mils. Essentially all of the concentration-penetration curve was cut

Table 2

Diffusion Couples and Diffusion Runs Used in This Investigation

Diffusion Run	Temperature °C	Time Hours	Couples	Components of Couples Nominal % Zn
3	780	361	025	0/10/0
			028	10/20/10
			033	0/20/0
			031	30/0/30
			029***	30/10/30
			024	30/20/30
4	855	323.5	037	0/10/0
			027	10/20/10
			034	0/20/0
			032	30/0/30
			035	30/10/30
			036	30/20/30
5	776	477.5	050	0/10/0
			030**	20/10/20
			048**	0/20/0
			051**	30/0/30
			041**	30/10/30
			039	30/20/30
6	855	479.5	046**	0/10/0
			044**	10/20/10
			047**	0/20/0
			042**	30/0
			040**	30/10/30
			038	30/20/30
7	724	431.5	052*	10/30
			055	20/30
8	854	92	061	0/10
			073	10/20
			056	0/20
			064	10/30
			066	20/30
9	783	94	059	10/20
			026	20/0/20
			062	10/30
			068*	20/30
10	915	39.75	049	0/30
			065	10/30
			069	20/30
11	914	114.3	060	0/10
			071	10/20
			057	0/20
12	887	114.2	043	0/30
			053	10/30
			067*	20/30

* This couple parted during machining and is not further reported.

** This couple was not machined for analysis and is not further reported.

*** One interface of this specimen parted. Data reported later are for the remaining couple which was sound.

into samples of 2-mil thickness. All of the cross-section was taken for the sample.

Distances were measured on the feed micrometer on the lathe; after every five cuts, an independent measurement was taken with a portable micrometer. In no case were the two independent measurements in disagreement by more than 1 mil over the total length of the specimens cut.

Upon approaching the wire interface, extra care was taken so as to observe the first appearance of the wires. Sketches were accurately drawn of the appearance of the wires on each interface (between two cuts) at which they could be seen. With 3-mil marker wires, it is possible to have them situated so that they appear at only one interface; slight displacement from this position will, however, cause the wires to be visible at two succeeding interfaces.

Two separate and distinct factors can cause the wires to appear in more than two interfaces: misalignment of the couple (wire interface not perpendicular to the axis) and a non-planar wire interface. Welded couples appear to be especially prone to the second fault; an extreme example can be seen in Fig. 1c. And, of course, despite all precautions, the first fault will appear in varying degrees.

However, the sketches made of the appearance of the wires allowed the wire interface plane to be determined within the limits of the procedure in all cases studied here. It is to be noted that this procedure will allow the determination of the interface plane to the closest 1 mil only; we can say, for example, that the wire interface lies within $1/2$ mil of the

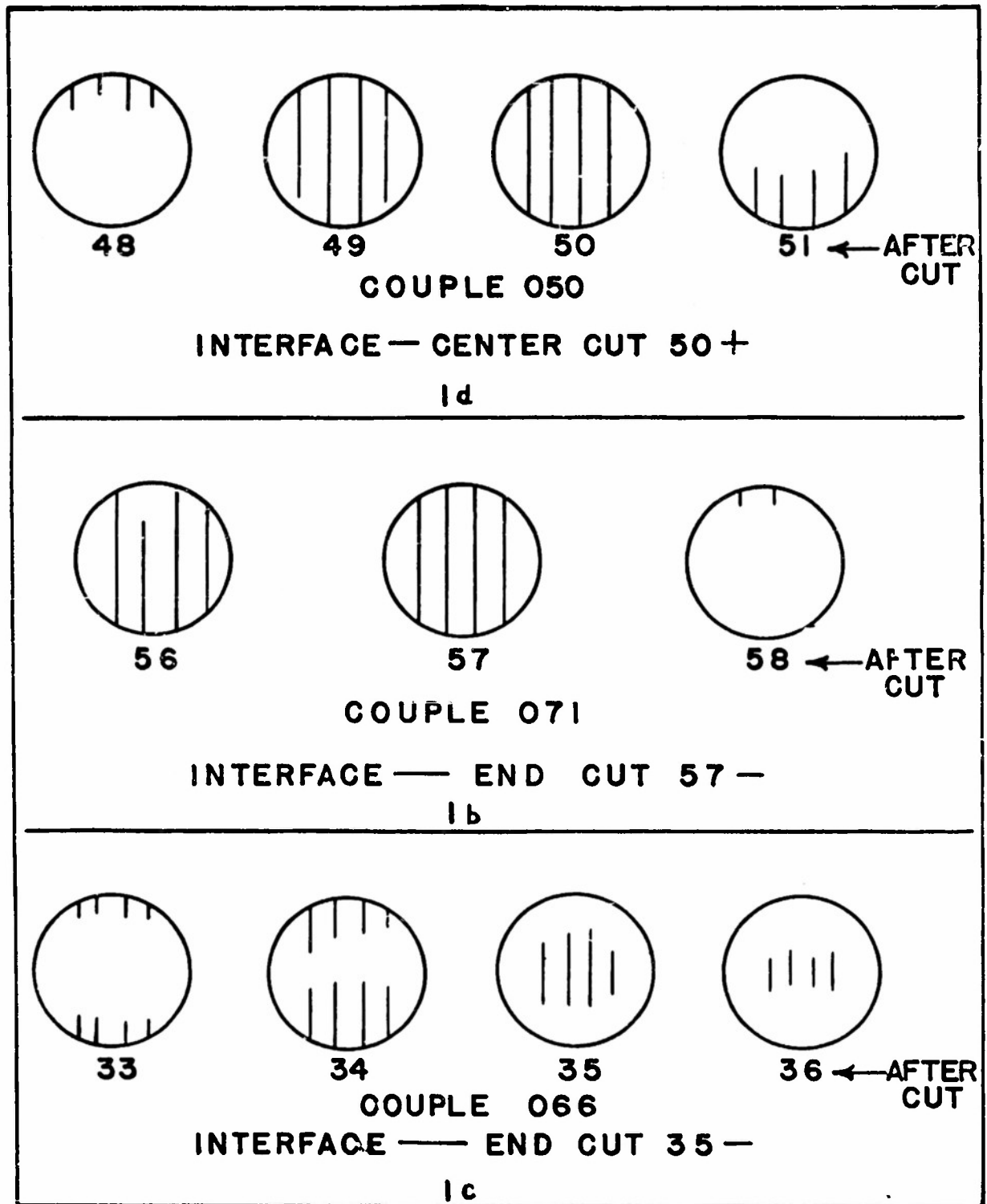


Fig. 1. Examples of appearance of wire interfaces.

interface after cut 68 or within 1/2 mil of the center cut 53. We can improve this only to the extent that we can say that the true position of the wire interface is more probably in one direction from this selected position than in the other; we can limit the uncertainty in the usual case to a total of 1/2 mil rather than $\pm 1/2$ mil. This is the basis for the positioning of the wire interface shown in Fig. 1.

As with all operations of this type, a certain element of luck is not to be discounted; the internal agreement of the results obtained in this manner, however, shows clearly what can be done by a careful machinist. But it cannot be emphasized too greatly that care in alignment and accuracy of sketches are necessary.

Chemical Analysis

Usually, every third machined sample was sent for chemical analysis. Samples were analyzed for copper by titration with thiosulphate using an outside iodine indicator. Those samples which were contaminated with tungsten, from the wires, were analyzed for both copper and zinc electrolytically and percent copper was calculated from these analyses. Analysis points that were in doubt were bracketed by two or three "fill-in" samples analyzed subsequently but in the same manner. The expected accuracy of these analyses was $\pm 0.2\%$ copper.

Certain random errors were encountered in these analyses for copper which made it, in some cases, difficult to decide what was in error and what was not. To answer these questions, and to give more firm foundation to all of the concentration-penetration curves, selected samples (six to ten per diffusion

couple) were sent for analysis by the electrodeposition method. This is, of course, a more reliable method, much less subject to error because of the smaller number of necessary operations. These few points on each diffusion curve were treated with greater confidence and served to define the curves with greater precision.

RESULTS

The results of the chemical analyses* were first plotted on 'probability' paper, as in Figure 2; this allows the drawing of smooth curves especially at the ends of the penetration curves, with greater justification than is possible when drawing the penetration curves directly. The smooth 'probability' curve was then transformed to regular rectangular coordinates and re-plotted as the usual concentration-penetration curve as in Figure 3. From these, D as a function of concentration was obtained from the Boltzmann-Matano solution. The values so obtained are listed in Tables 3-7 and plotted in Figure 4-6. Scatter among the individual diffusion coefficient values is in evidence, especially at the ends of the concentration range of any given sample; the diffusion coefficients vary more toward the high ends than they do at the low concentrations (with the exception of couple 031 and possibly 060). The effect of the 6⁰ temperature difference ca. 780°C is not discernible. There appears to be no evidence that D is not a single-valued function of the concentration; it appears that D is a single-valued

* Because of limitations of space, complete results of chemical analysis are not herein reproduced. For these data order Document _____ from American Documentation Institute 1719 N St., N. W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1" high on standard 35 mm. motion picture film) or \$1.05 for photocopies (6 x 8") readable without optical aid.

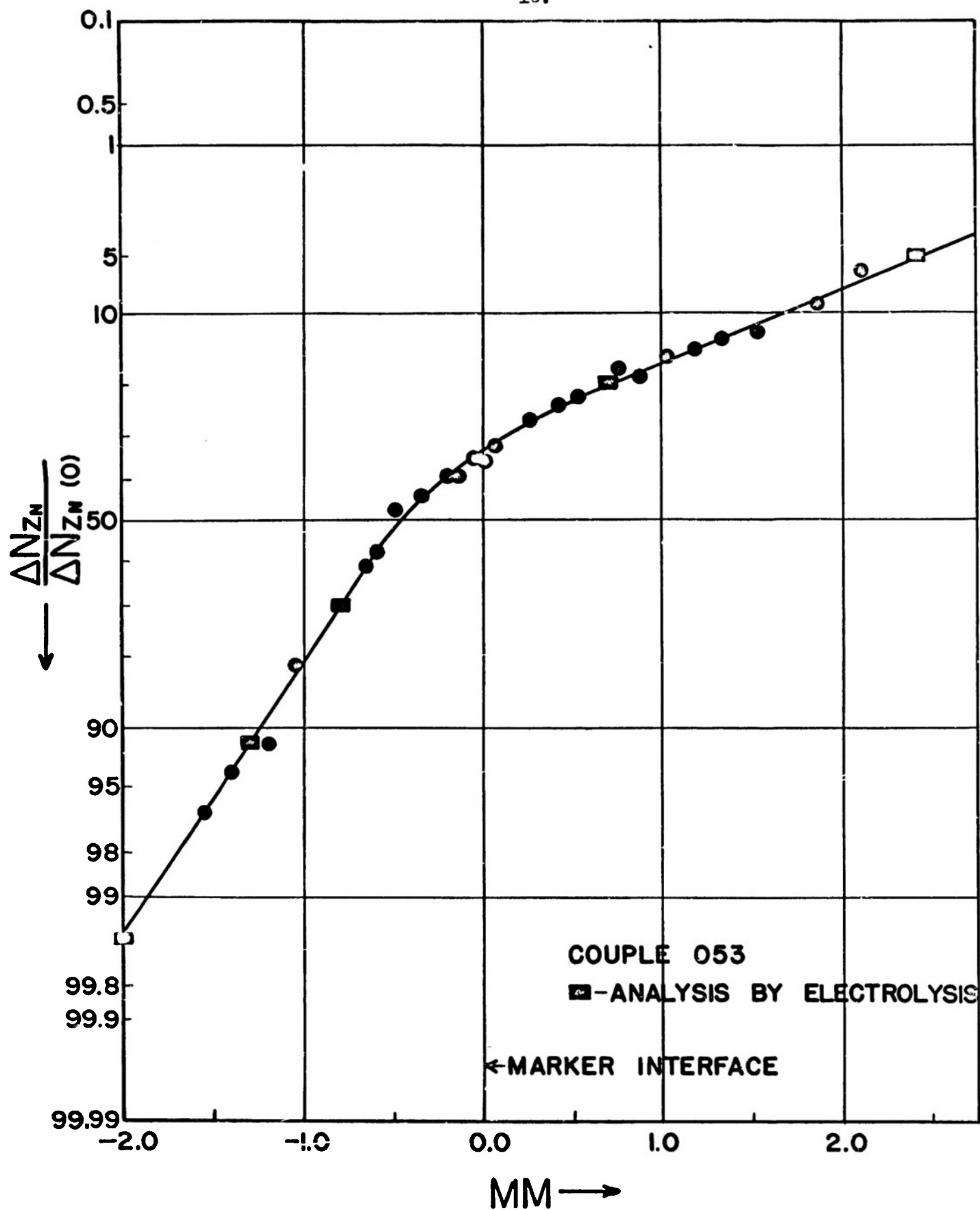


Fig. 2. Probability plot of data from couple 053 (10/30, 14402 hrs, 387°C).

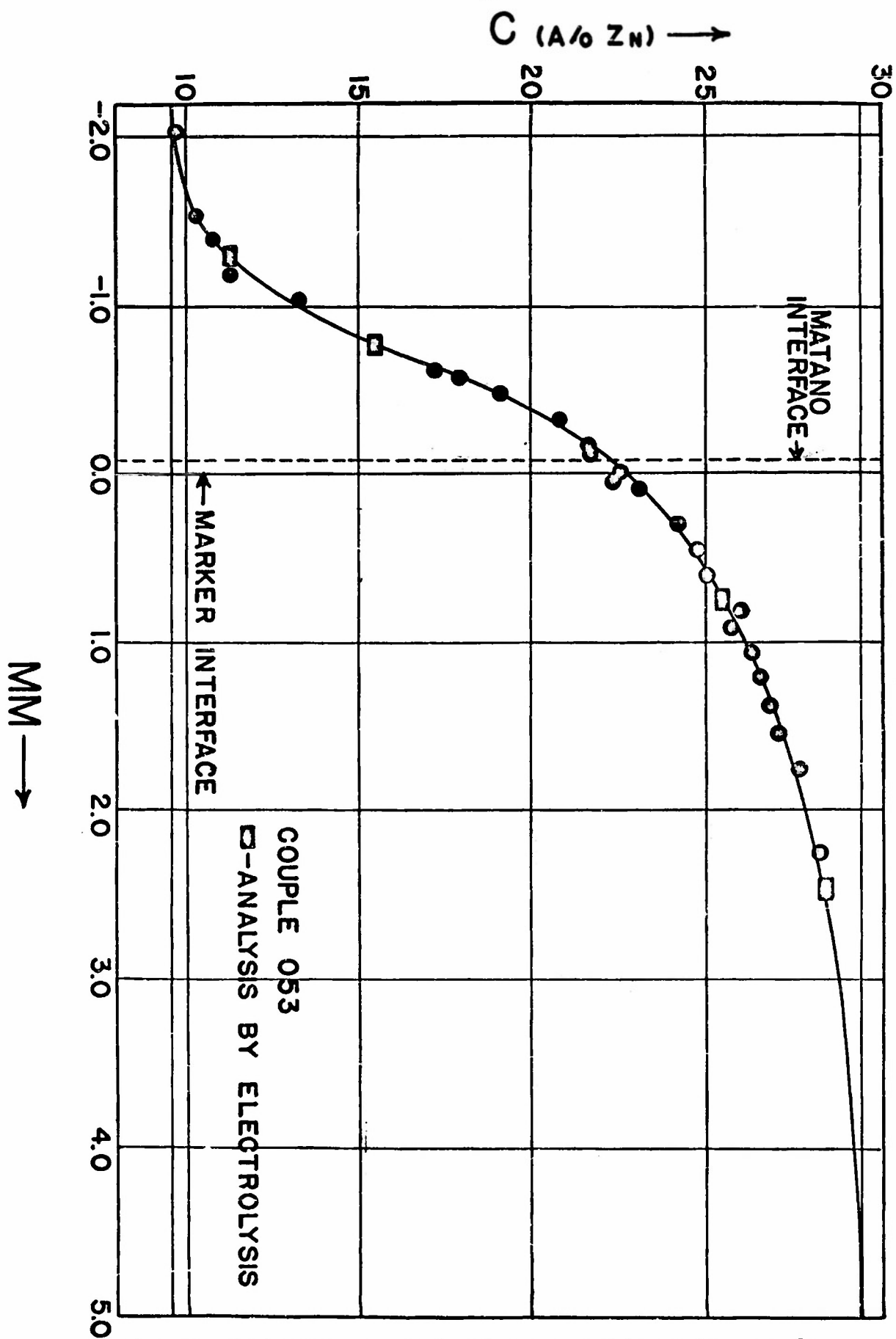


Fig. 3. Rectangular concentration-penetration curve, couple 053 (10/30, 144.2 hrs @ 887°C).

Table 3

$D(\text{cm}^2/\text{sec} \times 10^{-10})$ vs $C(\text{A/o Zn})$

$T = 724^\circ\text{C}$

A/o Zn	Couple 055 $T(^{\circ}\text{C}) = 724$	Composite
20	9.0	8.4
21	10.8	
22	11.9	11.8
23	15.8	
24	17.3	
25	21.6	22.0
26	29.6	27.0
27	34.6	
28	42.8	48.0
29	47.2	

Table 4

$D(\text{cm}^2/\text{sec} \times 10^{-10})$ vs $C(A/o \text{ Zn})$

T = ca 780°C

A/o Zn	Couple T°C	050 776	039 776	031 780	033 780	028 780	029 780	024 780	025 783	026 783	059 783	062 783	Composite
1		2.9		4.9	2.2				2.85	2.55			2.5
2		2.9		5.0	1.9				2.85	2.2			
3		2.9		4.4	2.3				2.85	2.9			
4		2.9		4.4	2.6				2.85	3.1			3.1
5		2.9		4.6	2.9				2.85	3.3			
6		2.9		4.9	3.3				2.85	3.5			
7		2.9		5.3	3.9				2.85	3.7			3.7
8		2.9		5.6	4.0				2.85	4.1			
9		2.9		5.4	4.8				2.85	4.6			
10				5.0	5.4	3.3	5.8			5.4	3.2	6.6	5.0
11				5.1	6.4	4.4	7.8			6.0	4.3	8.0	
12				6.2	7.5	4.8	8.3			6.5	4.9	7.3	6.8
13				9.7	8.2	5.7	7.7			7.5	5.4	7.5	
14				11.8	8.9	8.1	8.3			8.3	8.0	8.9	
15				12.5	9.4	10.3	9.2			9.0	10.3	9.4	10.4
16				14.2	11.5	12.2	10.6			9.5	13.3	11.8	12.0
17				16.1	12.9	13.7	12.7			11.7	14.5	14.0	
18				18.3	13.0	14.5	15.8			12.0	14.0	15.9	16.0
19				21.5	12.7	14.7	19.3			12.6	14.0	19.5	
20			21.3	25.1			22.2	19.6				22.2	22.0
21			21.6	28.0			26.2	22.5				25.8	
22			26.6	31.2			29.3	29.0				30.1	30.5
23			30.7	35.8			35.4	35.3				34.5	
24			40.0	39.7			39.7	40.0				41.3	
25			49.0	47.3			45.0	55.6				45.8	53.5
26			60.0	51.4			49.0	65.2				49.5	64.0
27			71.0	62.9			49.0	75.0				52.0	
28			80.0	46.2			48.4	92.5				52.0	107.5
29			74.0	38.9			50.3	89.0				49.4	

Table 5

 $D(\text{cm}^2/\text{sec} \times 10^{-9}) \text{ vs } C(A/o \text{ Zn})$

T = ca 855°C

A/o Zn	Couple ToC	061 854	056 854	073 854	064 854	066 854	032 855	037 855	034 855	027 855	035 855	036 855	Composite
1		0.97	1.1	1.8			0.84	0.89	1.1				1.0
2		0.98	1.2	2.0			0.99	0.94	1.1				
3		1.1	1.2	2.2			0.95	1.1	1.1				1.1
4		1.2	1.1	2.6			0.94	1.2	1.2				
5		1.3	1.2	3.1			1.0	1.2	1.2				
6		1.5	1.1	3.9			1.1	1.3	1.2				
7		1.6	1.2	4.6			1.3	1.4	1.3				1.4
8		1.65	1.3	4.8			1.5	1.6	1.4				
9		1.7	1.4	5.0			1.9	1.6	1.7	1.9			1.8
10			1.8	5.8			2.2	1.7	1.8	1.9	1.6		
11			2.5				2.2		2.2	2.1	2.1		
12				2.2			2.3		2.2	2.6	2.2		2.3
13			3.2	3.1			3.0		3.3	3.2	2.3		
14			3.7	3.9			3.6		3.6	3.8	3.0		3.6
15			4.0	4.6			3.8		4.1	4.2	4.1		4.1
16			4.4	4.8			4.2		4.1	5.0	5.1		5.4
17			4.5				4.8		4.2	5.5	5.6		
18			4.7	5.0			5.5		4.7	6.6	6.6		
19			4.7	4.8			6.2		3.9				
20						7.5	6.8			6.9	7.4		7.1
21						8.1	8.0			7.9	8.2		
22						8.5	9.2			9.9	9.7		9.6
23						9.9	11.6			11.8	11.1		
24						11.2	13.2			14.2	12.5		
25						13.0	15.1			16.1	15.5		15.0
26						16.1	17.2			19.0	18.6		18.0
27						22.0	20.0			20.6	20.9		
28						27.2	27.4			23.2	27.1		28.0
29						30.9	24.4			19.3	32.5		

Table 6

$D(\text{cm}^2/\text{sec} \times 10^{-9})$ vs $C(\text{A/o Zn})$

$T = 887^\circ\text{C}$

A/o Zn	Couple 043 $T^\circ\text{C}$ 887	Couple 053 $T^\circ\text{C}$ 887	Composite
1	1.2		1.8
2	1.6		
3	1.7		
4	1.7		
5	1.8		1.9
6	1.8		
7	1.8		
8	1.8		2.2
9	2.0		
10	2.6	4.0	3.0
11	3.4	4.8	
12	4.0	5.0	3.9
13	4.6	5.2	
14	5.5	5.2	
15	5.9	5.7	5.8
16	6.5	6.6	6.6
17	6.9	7.7	
18	7.6	8.9	8.8
19	8.8	10.8	
20	11.0	11.6	11.5
21	13.9	13.6	
22	15.5	17.0	15.0
23	18.6	21.9	
24	20.4	23.3	
25	23.6	27.9	23.2
26	25.0	30.2	27.2
27	26.0	32.0	
28	25.8	34.0	41.3
29	22.4	32.0	

Table 7

$D(\text{cm}^2/\text{sec} \times 10^{-9})$ vs $C(\text{A/o Zn})$

T = ca 915°C

A/o Zn	Couple T°C	060 914	057 914	071 914	049 915	065 915	069 915	Composite
1		1.4	2.3		2.7			2.6
2		1.5	2.0		3.3			
3		1.7	2.1		3.4			
4		2.5	2.4		3.3			
5		3.2	2.6		3.6			2.9
6		3.8	2.8		4.2			
7		4.1	3.1		4.1			
8		4.2	3.4		3.9			3.3
9		4.5	3.9		3.6			
10			4.5	5.2	4.8	4.9		4.6
11			5.0	4.8	5.8	5.8		
12			5.6	6.2	6.5	7.0		5.9
13			7.3	7.2	7.5	7.4		
14			8.3	8.2	8.5	7.7		
15			8.5	9.2	8.8	8.7		8.6
16			9.3	10.0	9.6	9.4		9.9
17			9.5	11.5	11.8	11.2		
18			11.8	12.3	13.5	13.9		13.0
19			9.5	10.3	15.3	16.0		
20					20.6	17.4	13.1	17.0
21					26.0	18.9	15.4	
22					28.4	20.9	20.3	21.6
23					30.3	29.4	25.2	
24					32.6	32.6	29.0	
25					37.5	35.5	32.5	32.5
26					42.8	39.6	38.5	38.0
27					47.5	44.8	40.4	
28					48.5	45.7	44.0	56.0
29					48.0	45.5	37.0	

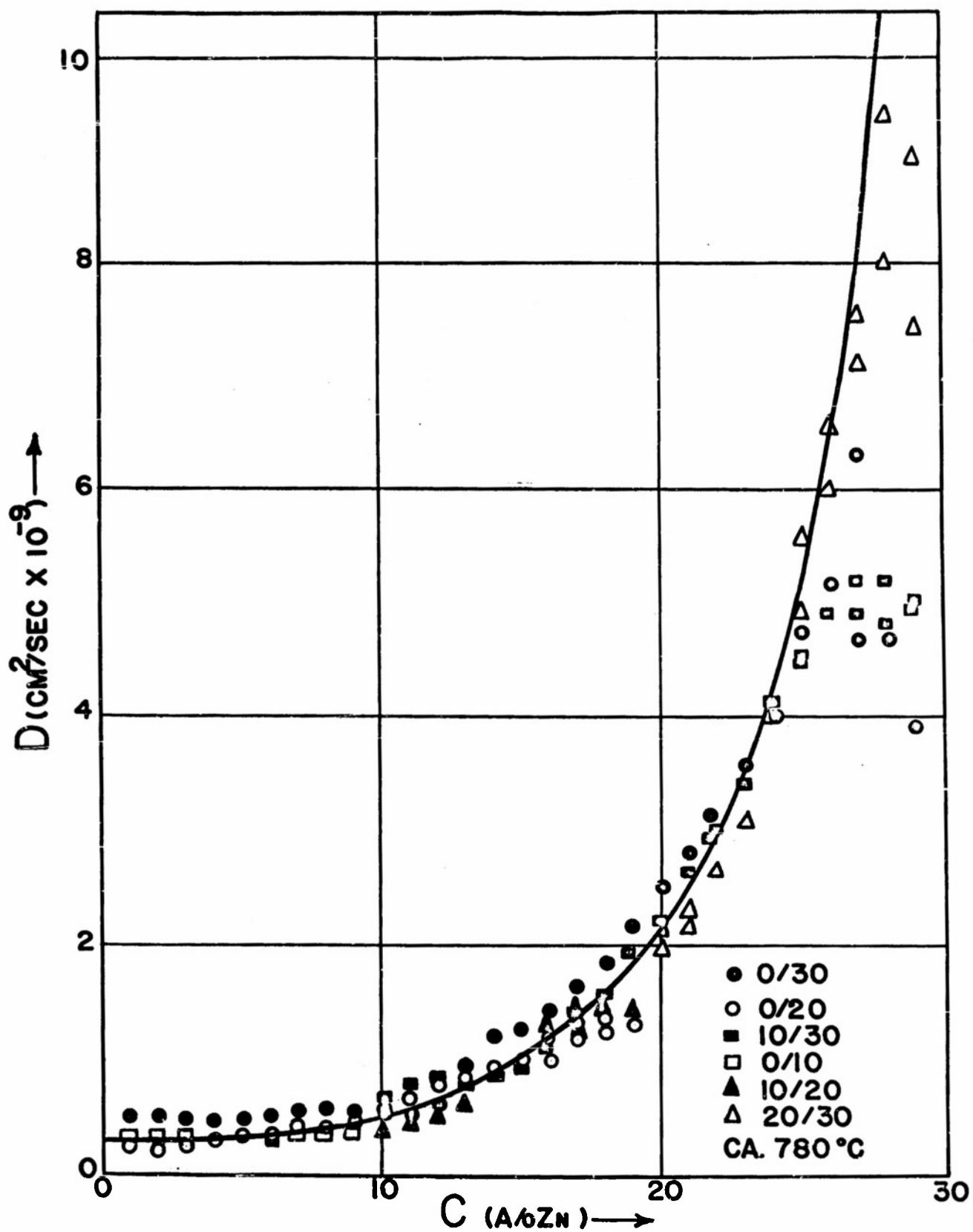


Fig. 4. General diffusion coefficient ^{vs} concentration, ca. 780°C.

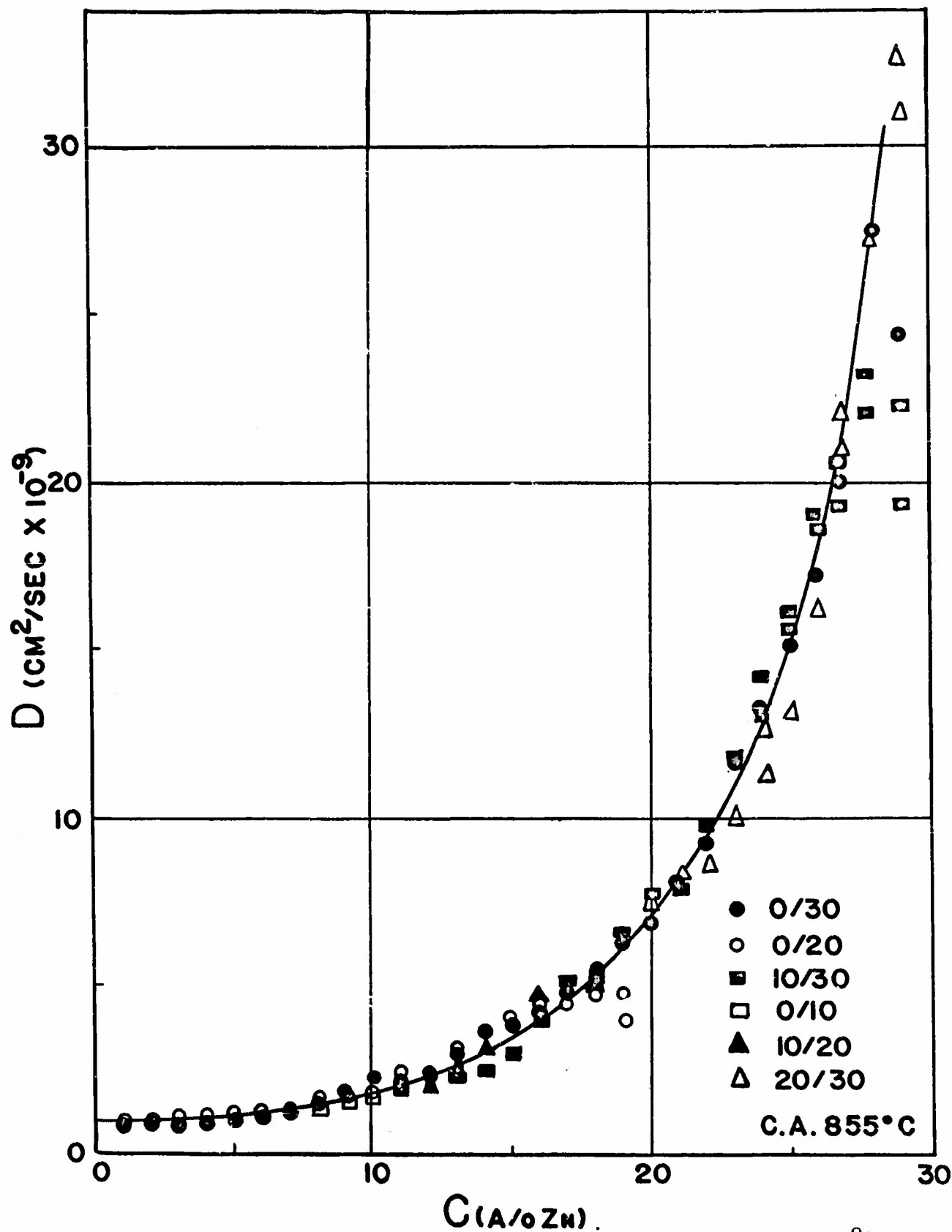


Fig. 5. General diffusion coefficient vs concentration, ca. 855°C.

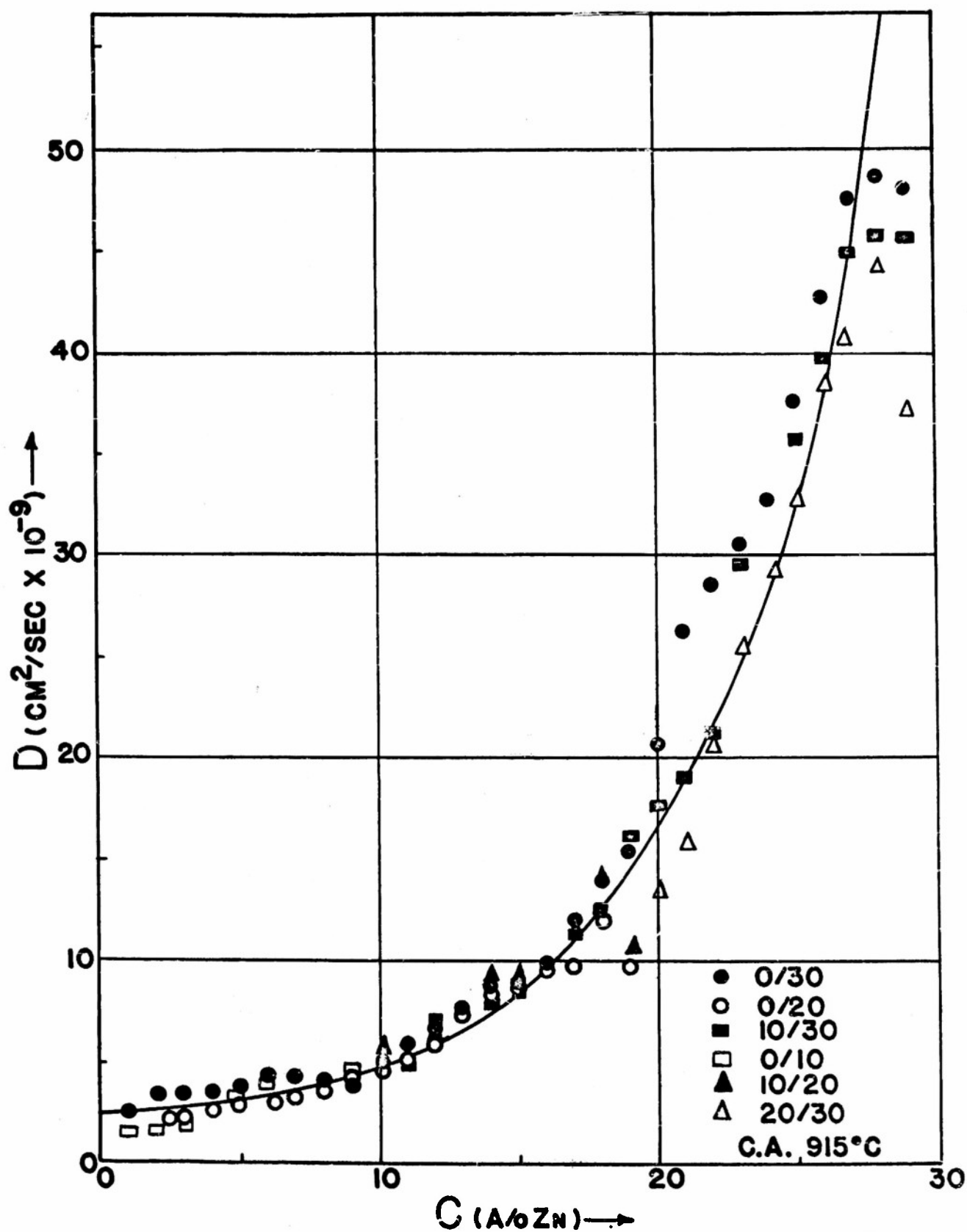


Fig. 6. General diffusion coefficient vs concentration, ca. 915°C

function of the concentration to within the limits of accuracy of the experimental methods used. This is the same result obtained by Wells et al¹⁴ for the diffusion of carbon in austenite.

On large-scale plots of the type of Figures 4-6, the functions $D(c)$ were drawn by inspection as smooth curves. Values of D were read at various concentrations from these curves and plotted as $\log_{10} D$ vs $1/T^{\circ}K$ as in Figure 7. The best straight lines were drawn through the points at given concentrations and these smoothed values appear as the 'composite' values in Tables 3-7 and the smooth curves in Figures 4-6. Calculated values of $Q(c)$ and $D_0(c)$ (from the Arrhenius equation in the form $D = D_0 e^{-Q/RT}$), are to be found in Table 8 and plotted in Figure 8.

The $Q(c)$ values are somewhat lower than those of da Silva and Mehl⁵, approaching theirs only at the higher zinc concentrations. The D_0 values show an unusual (and perhaps unlikely) passage through a maximum. Again they approach the values of da Silva and Mehl only at the higher zinc concentrations; the values show much less dependence on concentration than do those of the latter authors. But because of the large extrapolation involved, based on values determined over a very short range of temperature, little significance can be attached to these values.

Calculation of the Shift

The shift velocity was calculated on the basis of the finding of da Silva and Mehl that the shift is equal to the distance between the Matano (original) interface and the wire interface. The coordinates of the Matano interface have, of

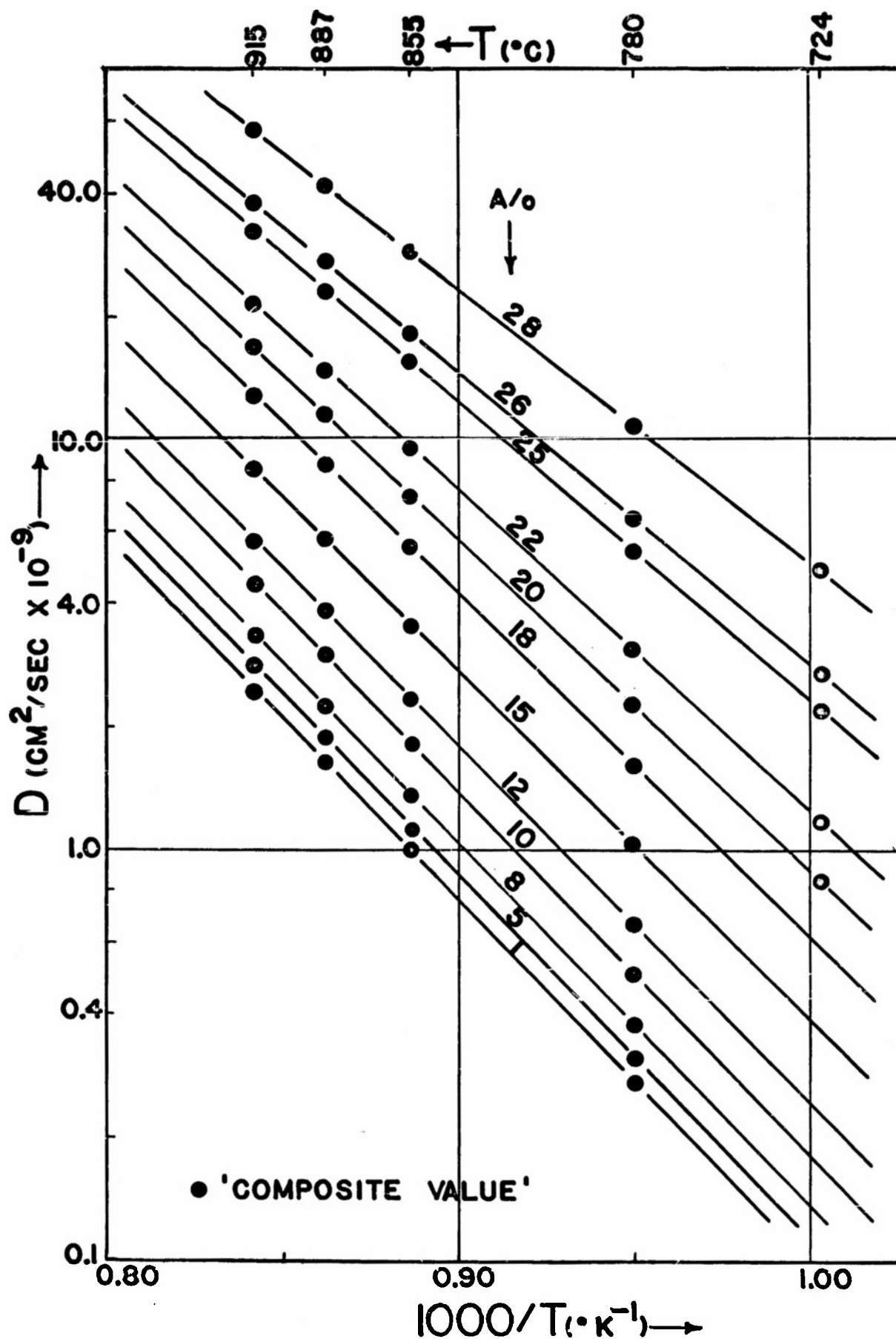


Fig. 7. Activation behavior vs composition for the 'composite' general diffusion coefficient.

Table 8

D₀ and Q Values as Functions of Concentration

A/o Zn	D ₀ (cm ² /secx10 ⁻²)	Q (K cal/mole)
1	5.6	40
5	6.2	40
8	6.2	39.5
10	8.3	39.5
12	9.4	39.2
15	8.3	38
16	9.5	38
18	10.1	37.5
20	9.0	36.5
22	6.6	35.2
25	3.1	32.5
26	2.9	32
28	1.6	29.7

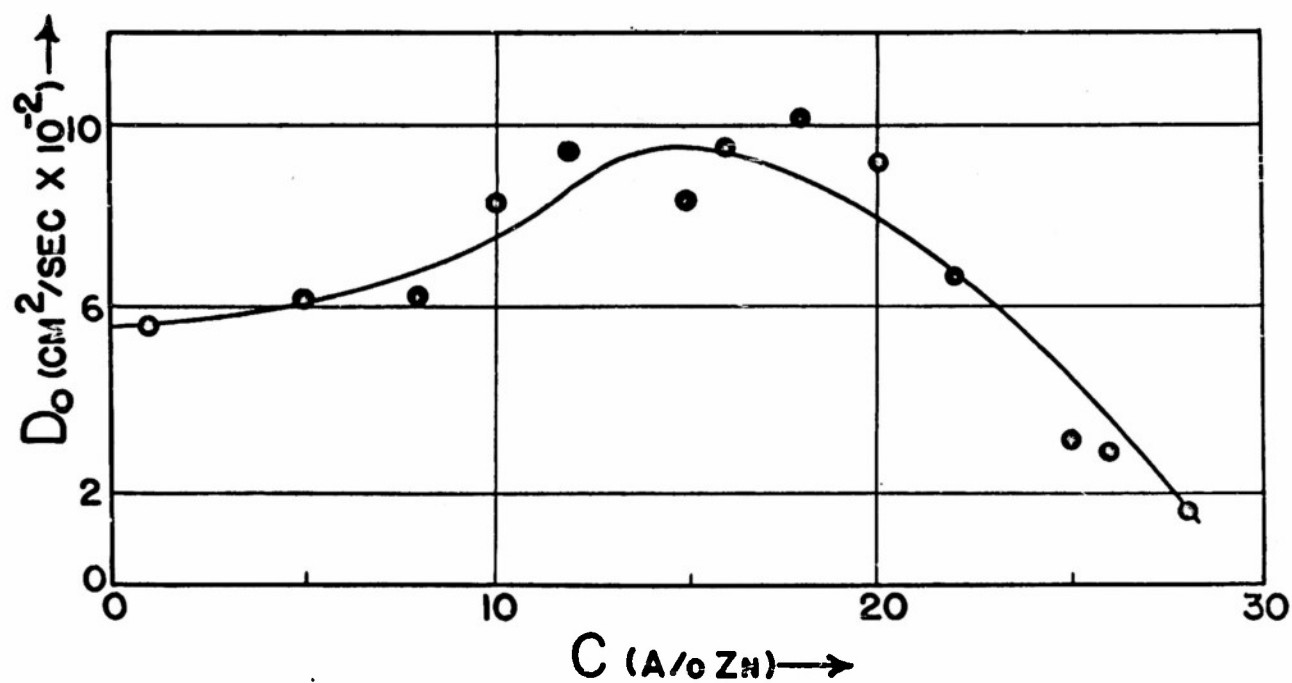
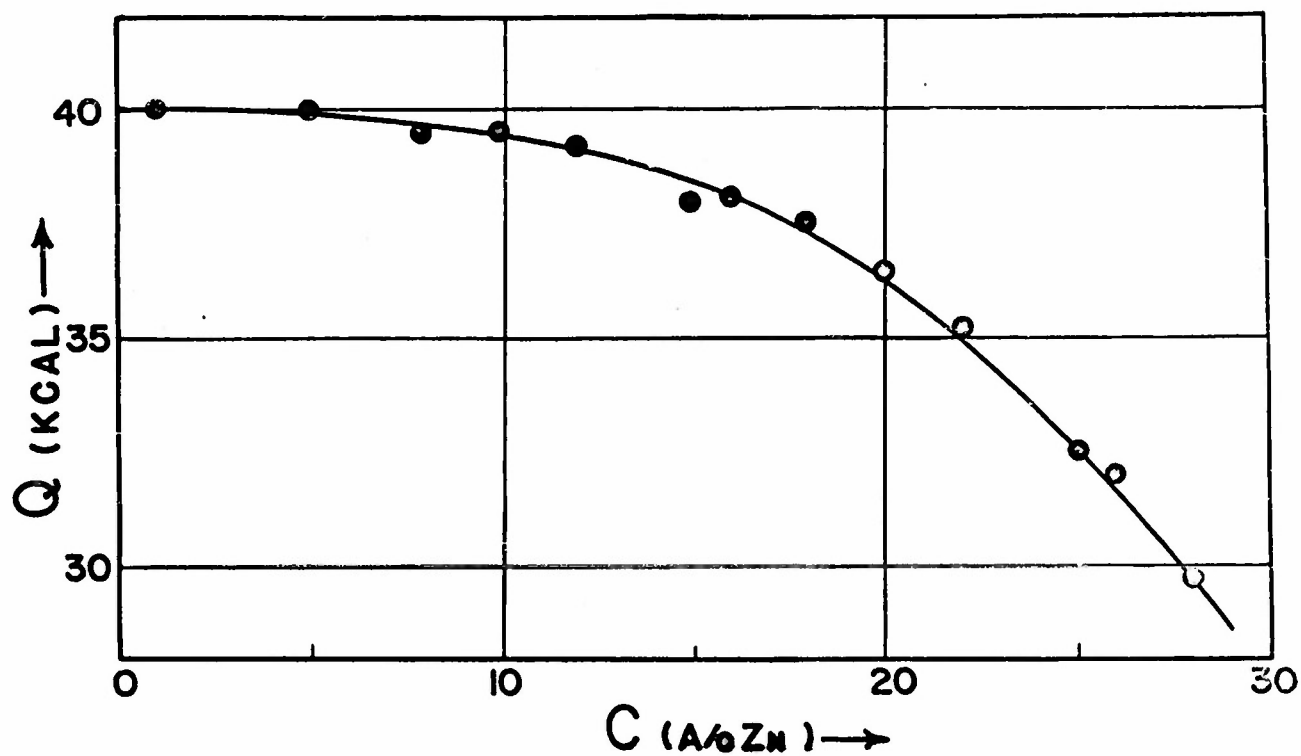


FIG. 8. Constants from the Arrhenius equation ($D = D_0 \exp(-Q/RT)$) vs concentration.

course, been calculated in connection with the calculation of D ; the wire interface position has been determined from the machining operation, but is known only to within $1/2$ mil. It is this range of $1/2$ mil which is shown in Table 9 - the value of 'shift' is that corresponding to the measured coordinate of the interface; the 'range' is $\pm 1/2$ mil depending on whether the expected deviation were forward or backward from the wire interface. Included in this table are values of the concentration at the wire interface and the concentration at the Matano (original) interface.

As can be seen from Table 9 the measured shifts vary up to 120×10^{-4} cm; many are under 50×10^{-4} cm. Under these conditions, this $1/2$ mil uncertainty must be cut down as the velocity of marker motion cannot be calculated if the position is in doubt by 50-100%.

We have accepted the finding of da Silva and Mehl that, independent of temperature, the shift is a linear function of the Matano area; we do not know, but may suspect, that this relationship is also independent of composition range in a given system. Plots of this type can be found in Figures 9-15; the first six for a given concentration range, the last for all couples here studied. Within a given concentration range there is no apparent deviation from the da Silva relationship; there is, however, a trend within the total range so that it appears that the slopes vary with the range. We shall accept this for the moment, returning to Figure 15 later.

Figures 9-14 do serve to limit the possible extent of the shift sharply; the remaining uncertainty has been arbitrarily

Table 9

Derived Data (Raw) for All Couples

Couple Type	Couple	T°C	t Hours	A _{Mat} A/o-cm x10 ⁻⁴	C _{wire} A/o Zn	C _{Mat} A/o Zn	Shift cmx10 ⁻⁴	Range
0/10	050	776	477-1/2	1325	5.0	5.0	0.0	12.7
	025	780	361	1065	5.0	5.0	0.0	12.7
	061	854	92	1130	5.2	5.2	1.4	14.1
	037	855	323-1/2	2160	5.2	5.2	0.0	12.7
	060	914	114-1/3	1910	5.6	5.6	1.5	14.2
10/20	028	780	361	1910	15.35	15.3	6.8	19.5
	059	783	94	985	15.35	15.3	1.1	13.8
	073	854	92	1900	15.1	15.1	0.1	12.6
	027	855	323-1/2	3640	15.25	15.2	5.3	18.0
	071	914	114-1/3	3290	15.0	15.0	16.6	3.9
0/20	033	780	361	3050	11.65	11.2	30.2	17.5
	026	783	94	1570	11.65	11.2	13.1	0.4
	056	854	92	3020	12.2	11.75	28.2	15.5
	034	855	323-1/2	5600	12.2	11.7	53.2	40.5
	057	914	114-1/3	4990	12.15	11.7	42.4	29.7
20/30	055	724	431-1/2	2530	25.45	25.3	26.6	13.9
	039	776	477-1/2	5025	25.25	25.2	38.6	25.9
	024	780	361	4600	25.3	25.25	25.5	38.2
	066	854	92	3900	25.4	25.25	35.0	22.3
	036	855	323-1/2	7850	25.4	25.3	67.0	54.3
	038	855	479-1/2	8775	25.4	25.3	56.0	69.7
	069	915	39-3/4	3720	25.1	25.0	27.6	40.3
10/30	029	780	361	6290	22.3	21.8	51.5	38.8
	062	783	94	3230	22.2	21.8	33.9	21.2
	064	854	92	5880	22.65	22.3	42.3	55.0
	035	855	323-1/2	10950	22.75	22.4	83.3	96.0
	053	887	114-1/2	9025	22.75	22.3	80.4	67.7
	065	915	39-3/4	6470	22.2	21.8	52.9	40.2
0/30	031	780	361	7900	20.15	19.2	76.6	63.9
	032	855	323-1/2	13650	20.8	19.8	116.8	129.5
	043	887	144-1/2	10790	20.3	19.4	89.0	101.7
	049	915	39-3/4	7670	20.65	19.9	60.9	73.6

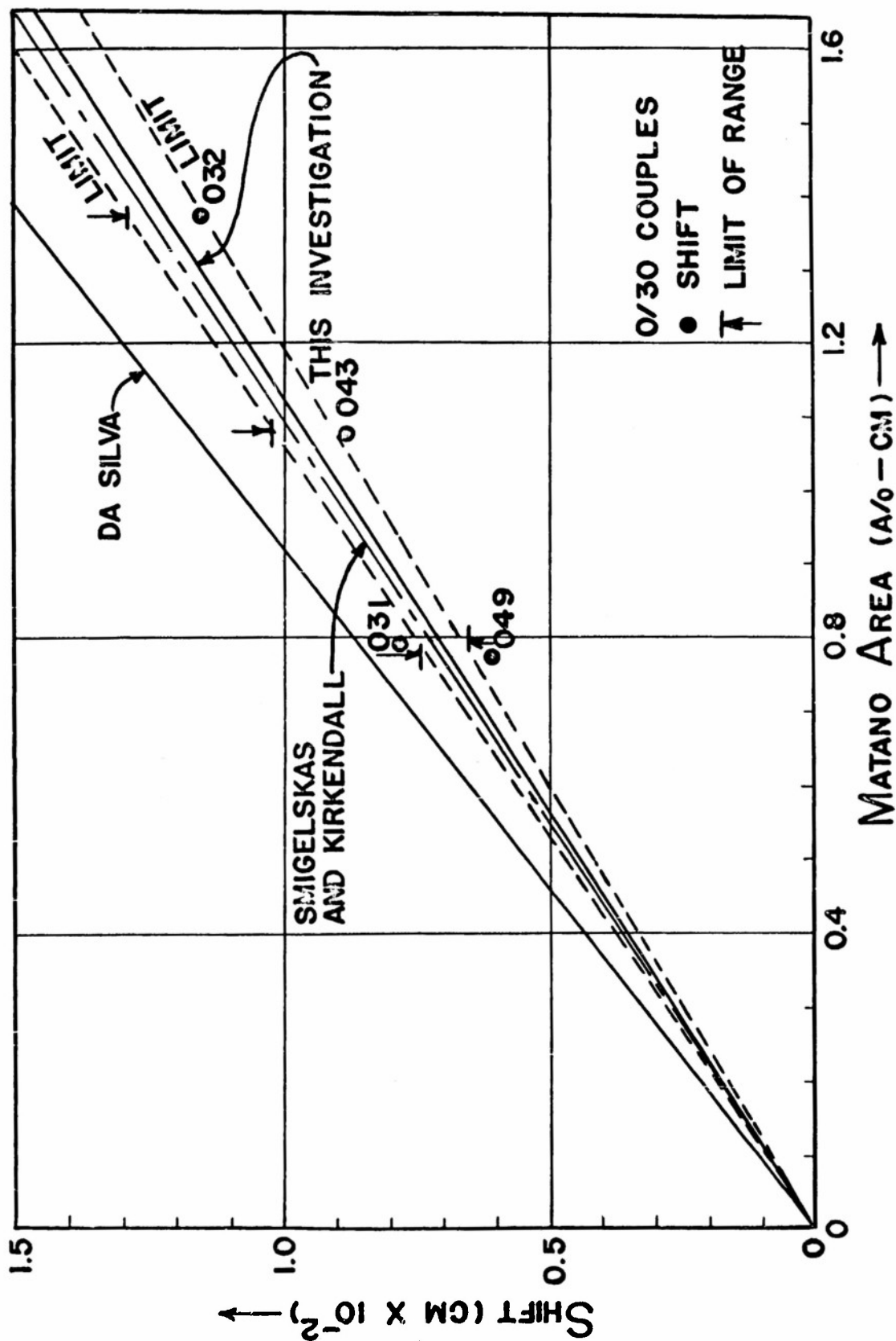


Fig. 9. Shift vs Matano Area, O/30 couple.

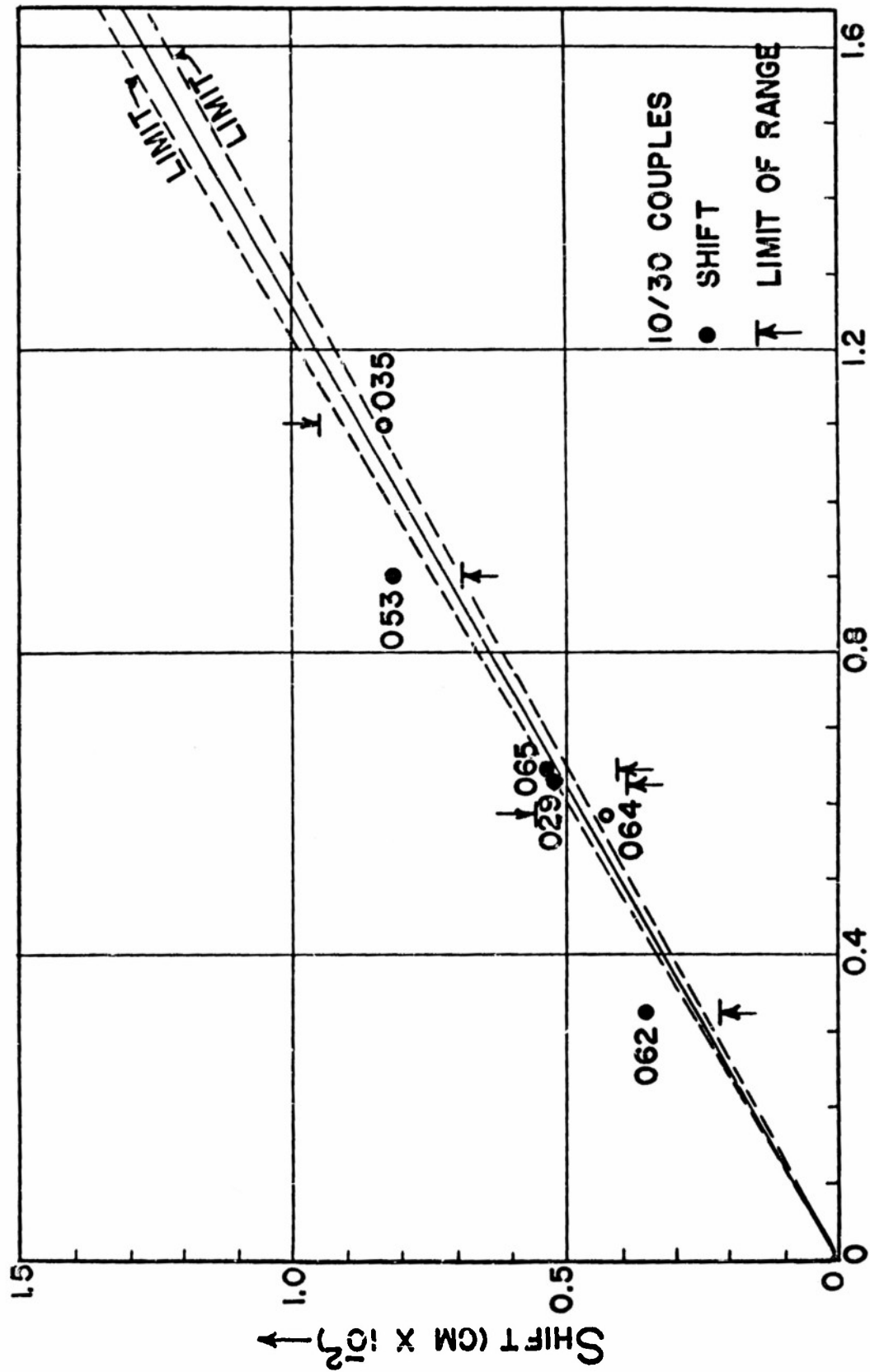


Fig. 10. Shift vs Matano Area, 10/30 couples.

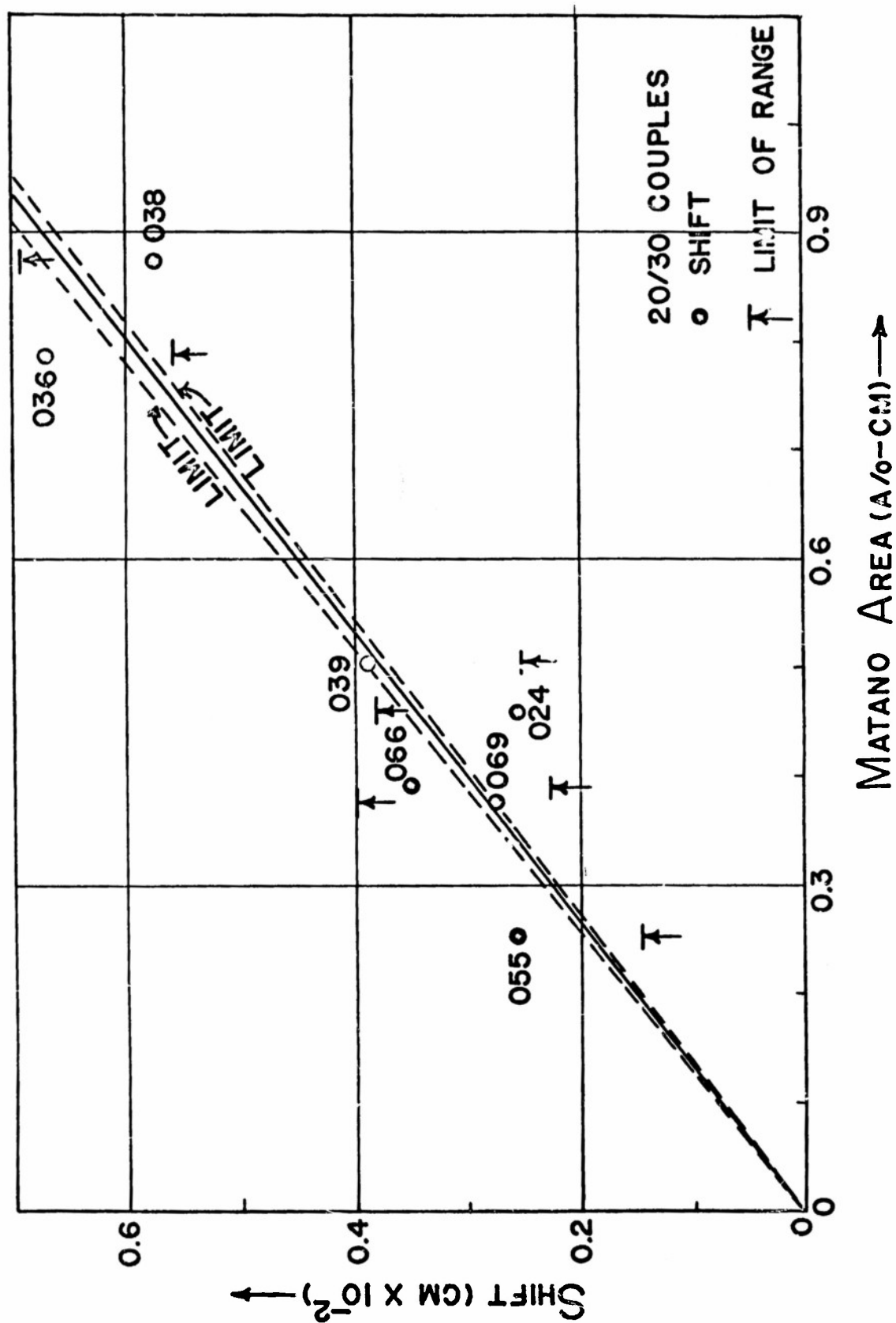


Fig. 11. Shift vs Matano Area, 20/30 couples.

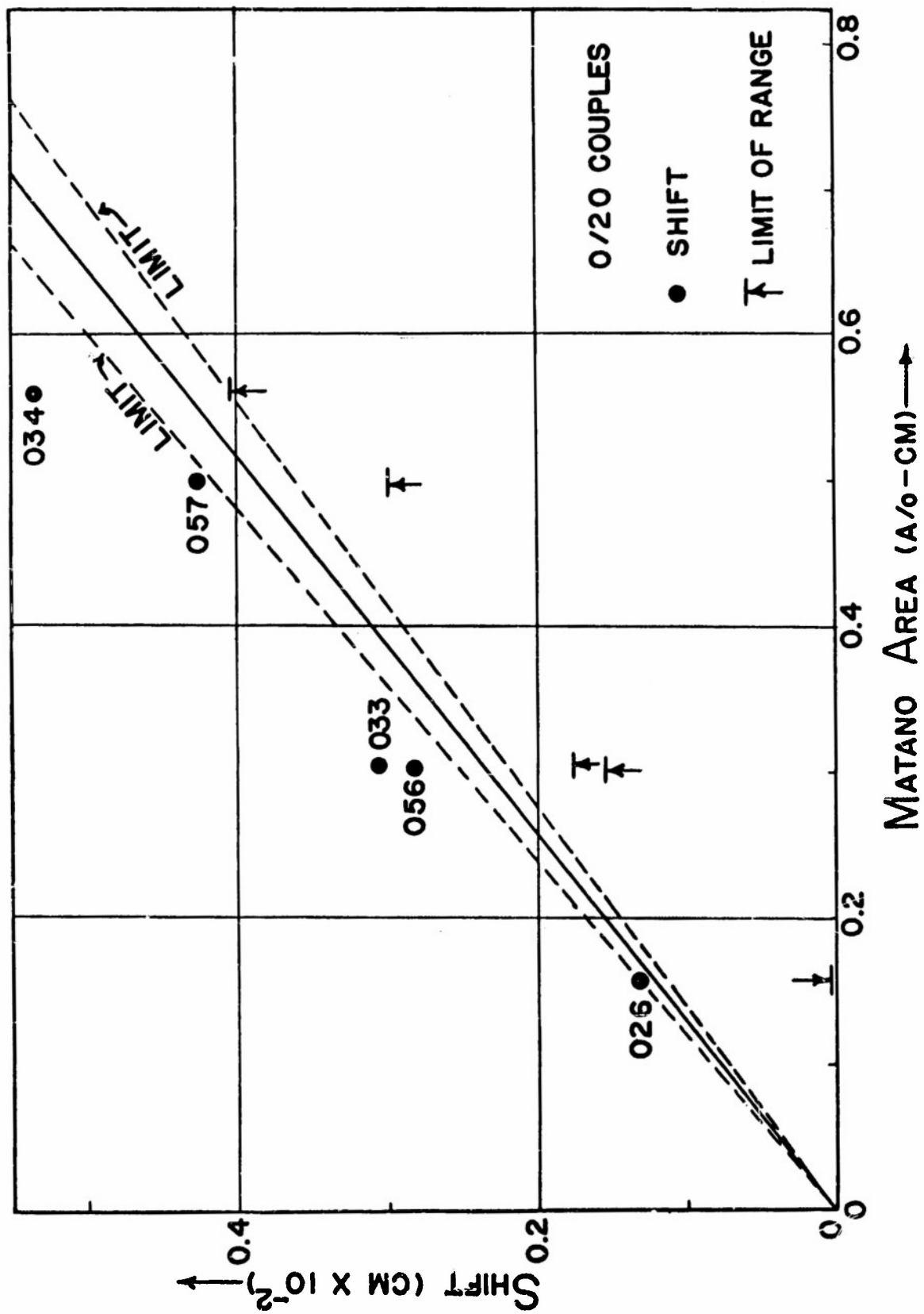


Fig. 12. Shift vs Matano Area, 0/20 couples.

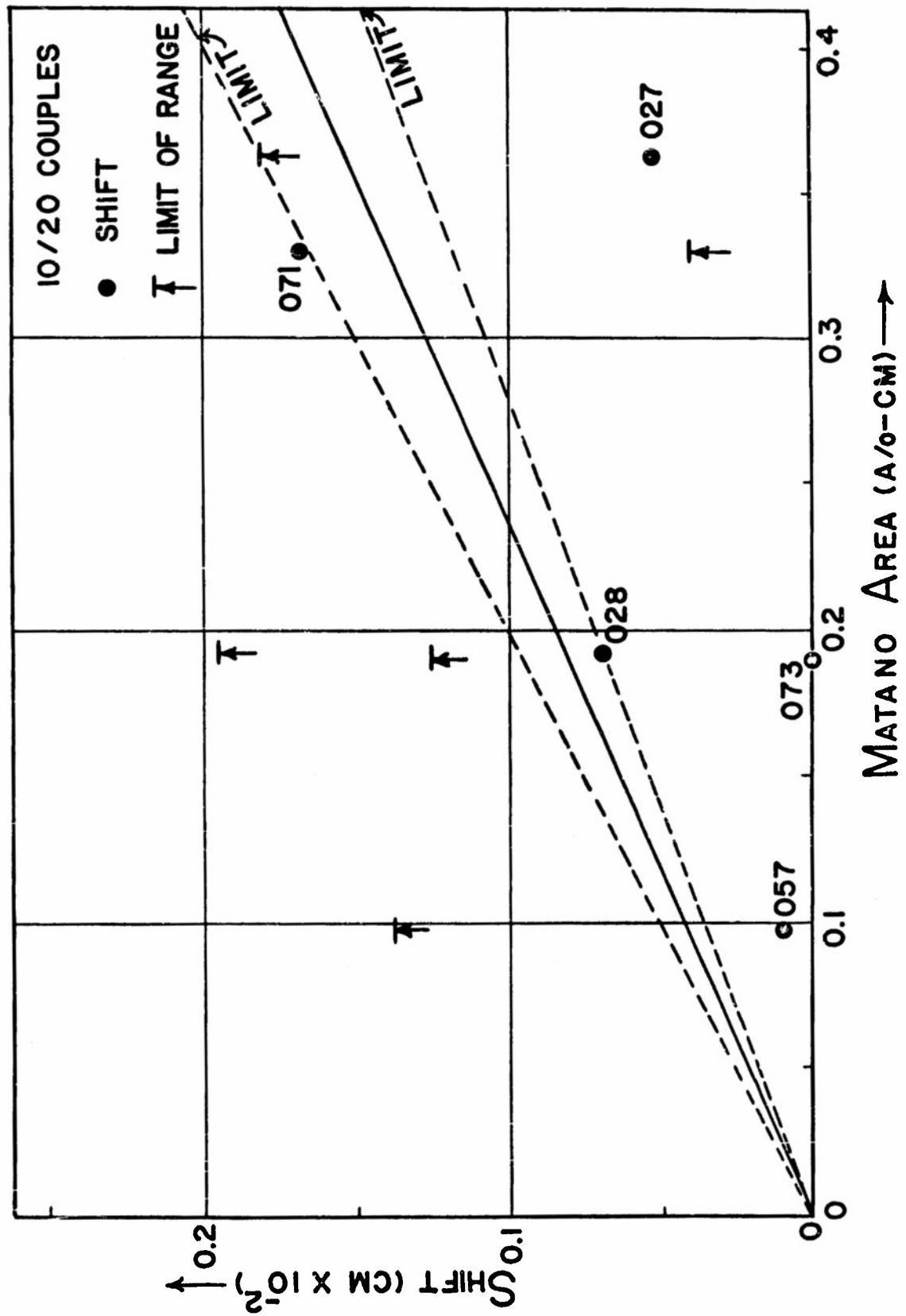


Fig. 13. Shift vs Matano Area, 10/20 couples.

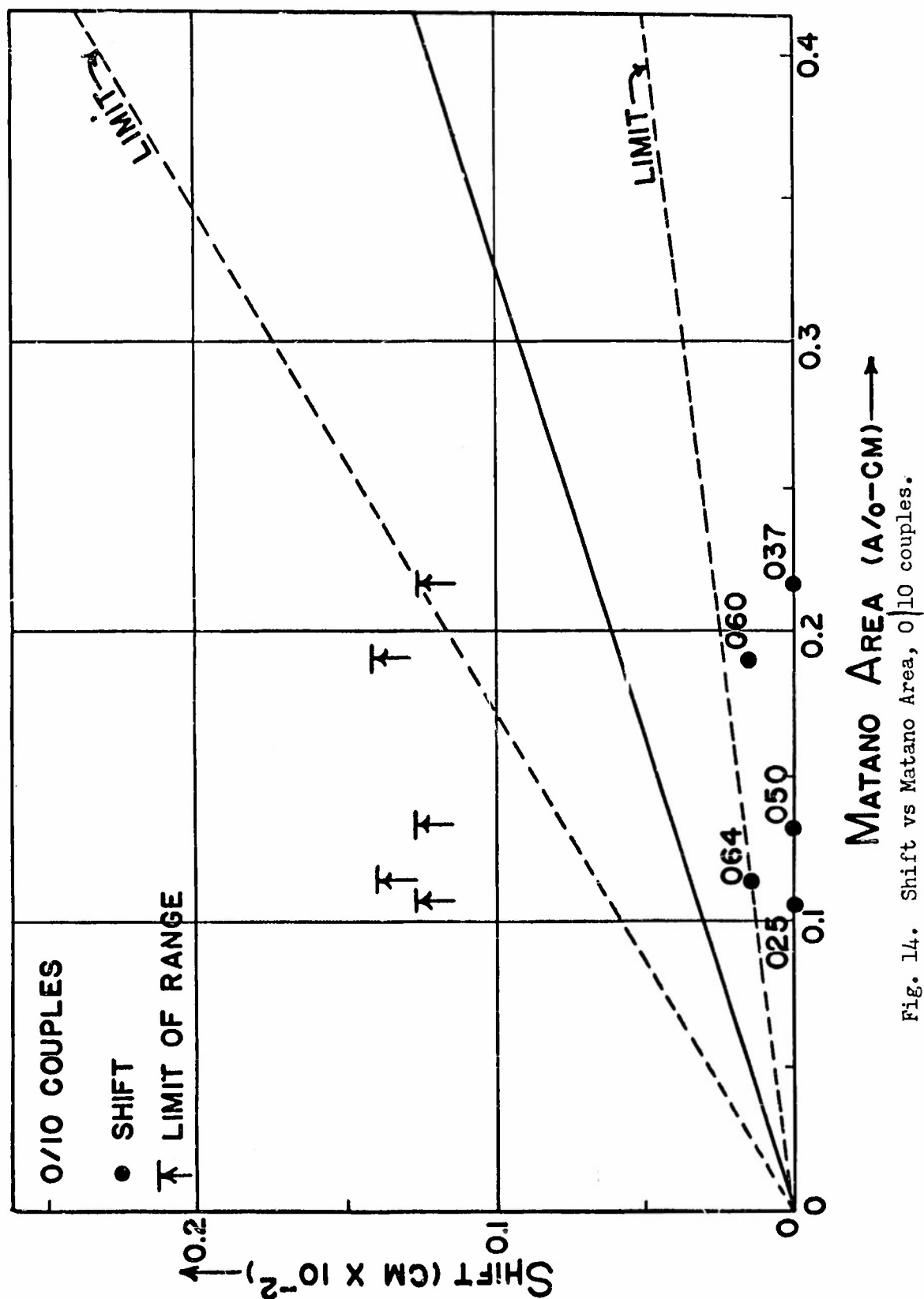
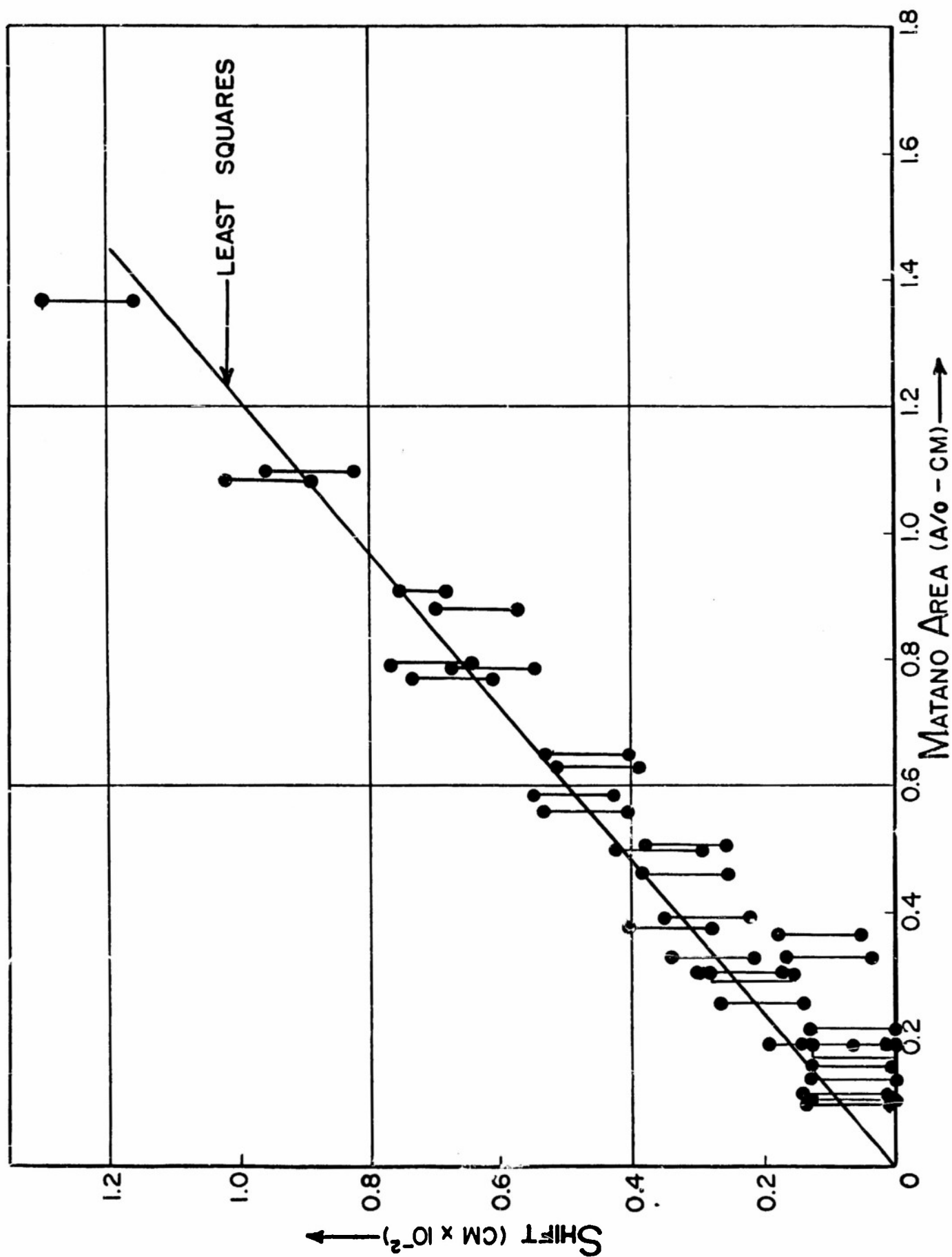


Fig. 14. Shift vs Matano Area, 0/10 couples.



bisected to give the constant relating shift to Matano area.

If the values of shift are selected from these plots, it is implicitly assumed that the measured Matano areas are accurate and correct. But, in view of the scatter in D-values found above, it would appear that this is not the case - some of this scatter must be due to inaccuracies in measurements of areas and, more important, to inconsistencies among the plotted concentration-penetration curves. We may check this and remove some of the uncertainties by plotting the logarithm of the measured Matano area divided by $(\text{time})^{1/2}$, (a rate-like constant) against $1/T$ in a given concentration range. This has been done in Figure 16. It will be seen that, in a few cases, this procedure leads to a much improved approximation to the Matano area.

To be as accurate as possible, the data of Figures 9-15 should now be replotted utilizing the more accurate Matano area values; in practice, however, the slopes are quite insensitive to the smoothed Matano areas; in the present case, none of the Matano areas which were inconsistent were 'critical' - they did not serve as limiting values for the slope. It is sufficient, then, to read from Figures 9-14 the shift corresponding to the smoothed Matano area for this couple. It is these values which are reported in Table 10 together with the measured tangents to the concentration-penetration curves at the wire interface, which are necessary in calculating the separate diffusivities. The values given for shift in the 0/10 couples and, to some extent, in the 10/20 couples are quite arbitrary. The possible limits for the shift 'rate' as seen in

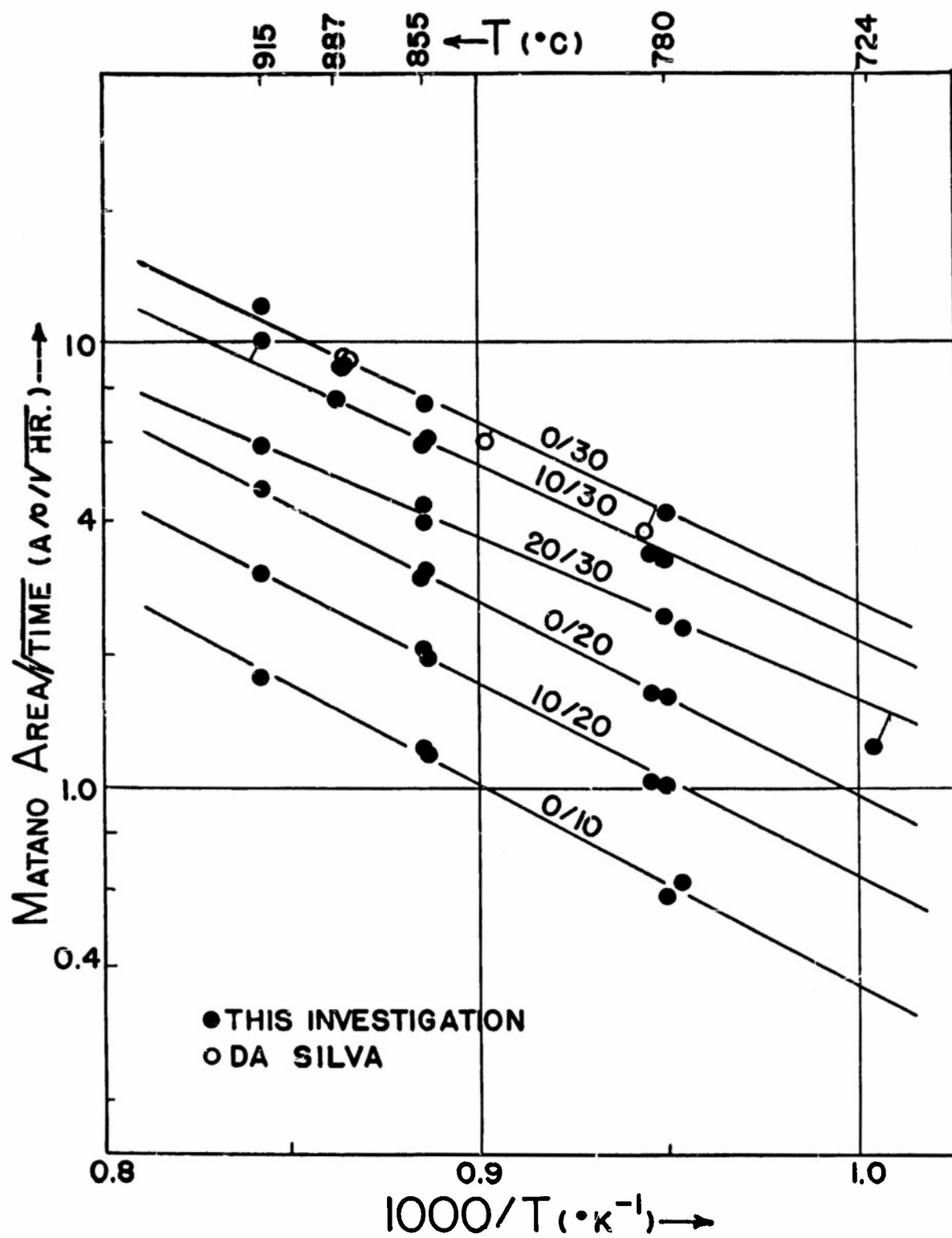


Fig. 16. Activation behavior vs composition for the Matano Area / (time)^{1/2}.

Table 10

Derived Data (Smoothed) for All Couples

Couple Type	Couple	$\frac{A_{Mat}}{A/o-cm} \times 10^{-4}$	$\frac{C_{Mat}}{A/oZn}$	Shift cm $\times 10^{-4}$	$(\frac{dN_{Zn}}{dx})_w$ cm ⁻¹
0/10	050	1280	5.2	3.8	1.26
	025	1140		3.4	1.38
	061	1115		3.35	1.25
	037	2105		6.3	0.640
10/20	028	1975	15.2	8.1	0.904
	059	1040		4.5	1.22
	073	1870		7.7	0.701
	027	3525		14.5	0.399
	071	3240		13.3	0.434
0/20	033	3020	11.5	23.5	1.46
	026	1580		12.2	2.99
	056	2880		22.3	1.52
	034	5415		42.2	0.866
	057	5000		38.8	1.08
20/30	055	3180	25.2	24.0	0.285
	039	5090		38.0	0.281
	024	4555		34.5	0.294
	066	3870		29.2	0.399
	036	7335		55.0	0.213
	038	8910		67.0	0.1845
	069	3685		27.5	0.391
10/30	029	6455	22.1	51.0	0.792
	062	3495		28.0	1.53
	064	5760		45.5	0.792
	035	10850		86.0	0.4025
	053	9060		71.5	0.524
	065	5670		45.0	0.818
0/30	031	7885	19.6	70.5	1.18
	032	13600		122.5	0.911
	043	11280		101.0	0.836
	049	7180		64.0	1.08

Figures 13-14 are widespread; long-time diffusion runs are needed to limit this range. The concentration at the Matano interface listed in Table 10 is an average of the values listed in Table 9. There is, apparently, no consistency in the values for either the marker concentration or the Matano interface concentration; this is in agreement with the observations of Thomas and Birchenall¹⁹.

Calculation of the Individual Diffusion Coefficients,
 D_{Zn} and D_{Cu}

Darken's equations for the determination of the individual diffusion coefficients, written in terms of the general diffusion coefficient, D (the Boltzmann-Matano D), the coordinates of the marker, x_m , the fractional concentration, N , the tangent to the concentration-penetration curve at the marker, $\left(\frac{dN}{dx}\right)_m$, and the time, t , are

$$D = N_{Zn} D_{Cu} + N_{Cu} D_{Zn}$$

$$\frac{x_m}{2t} = (D_{Zn} - D_{Cu}) \left(\frac{dN_{Zn}}{dx}\right)_m$$

The D which was used was the 'composite' D previously reported and obtained at an average wire concentration; the tangents were measured at the observed wire interfaces. Computed values of D_{Zn} and D_{Cu} , the difference $D_{Zn} - D_{Cu}$, and the ratio D_{Zn}/D_{Cu} are reported in Table 11 with the appropriate D 's and are shown in Figures 17-19, the difference $D_{Zn} - D_{Cu}$ is shown in Figure 20; activation plots are shown in Figures 21 and 22.

Several points appear immediately. It can be seen that the values of D_{Zn} behave quite regularly, even in activation plot;

Table 11
Computed Values of the Individual Diffusion Coefficients

Couple	Cw	A/oZn	RAW				SMOOTHED			
			D cm ² /sec x10 ⁻⁹	D _{Zn} cm ² /sec x10 ⁻⁹	D _{Cu} cm ² /sec x10 ⁻⁹	D _{Zn} -D _{Cu} cm ² /sec x10 ⁻⁹	D _{Zn} cm ² /sec x10 ⁻⁹	D _{Cu} cm ² /sec x10 ⁻⁹	D _{Zn} -D _{Cu} cm ² /sec x10 ⁻⁹	D _{Zn} -D _{Cu} cm ² /sec x10 ⁻⁹
050			0.29	0.30	0.21	0.09	0.30	0.047	0.25	0.25
025			0.31	0.32	0.22	0.09	0.32	0.050	0.27	0.27
061	5.2		1.14	1.16	0.75	0.42	1.19	0.200	0.96	0.96
037			1.15	1.17	0.75	0.42	1.20	0.203	0.965	0.965
030			2.80	2.85	1.83	1.02	2.92	0.550	2.37	2.37
028			1.07	1.12	0.78	0.34	1.225	0.210	1.015	1.015
059			1.15	1.23	0.70	0.53	1.315	0.225	1.09	1.09
073	15.2		3.70	3.95	2.30	1.66	4.225	0.770	3.45	3.45
027			3.75	3.98	2.46	1.52	4.28	0.780	3.48	3.48
071			8.80	9.37	5.65	3.72	10.03	1.95	8.08	8.08
033			0.66	0.735	0.12	0.62	0.730	0.126	0.605	0.605
026			0.70	0.77	0.17	0.60	0.777	0.135	0.642	0.642
056	12.0		2.35	2.62	0.40	2.22	2.60	0.490	2.11	2.11
034			2.40	2.65	0.56	2.09	2.66	0.500	2.16	2.16
057			5.75	6.28	1.91	4.36	6.35	1.32	5.03	5.03
055			2.30	2.99	0.25	2.72	2.795	0.835	1.96	1.96
039			5.30	6.30	2.36	3.94	6.35	2.20	4.15	4.15
024			5.60	6.74	2.20	4.52	6.72	2.30	4.42	4.42
066	25.3		16.0	18.8	7.6	11.1	19.1	6.90	12.2	12.2
036			16.1	18.9	7.7	11.1	19.2	7.00	12.2	12.2
038			16.1	18.8	8.1	10.6	19.2	7.00	12.2	12.2
069			34.0	40.2	15.4	24.7	40.2	15.7	24.5	24.5
029			3.30	3.92	1.20	2.72	3.95	1.05	2.90	2.90
062			3.50	4.11	1.40	2.71	4.20	1.10	3.10	3.10
064	22.5		10.3	12.3	3.55	8.70	12.3	3.50	8.78	8.78
035			10.4	12.5	3.3	9.20	12.4	3.57	8.80	8.80
053			16.0	19.0	5.8	13.1	19.0	5.70	13.3	13.3
065			23.0	27.4	8.1	19.3	27.3	8.30	19.0	19.0
031			2.40	2.87	0.57	2.30	2.87	0.57	2.30	2.30
032			7.80	8.99	3.20	5.78	9.30	2.00	7.30	7.30
043	20.5		12.4	14.8	3.20	11.6	14.75	3.20	11.55	11.55
049			18.0	22.2	1.50	20.7	21.4	4.75	16.65	16.65

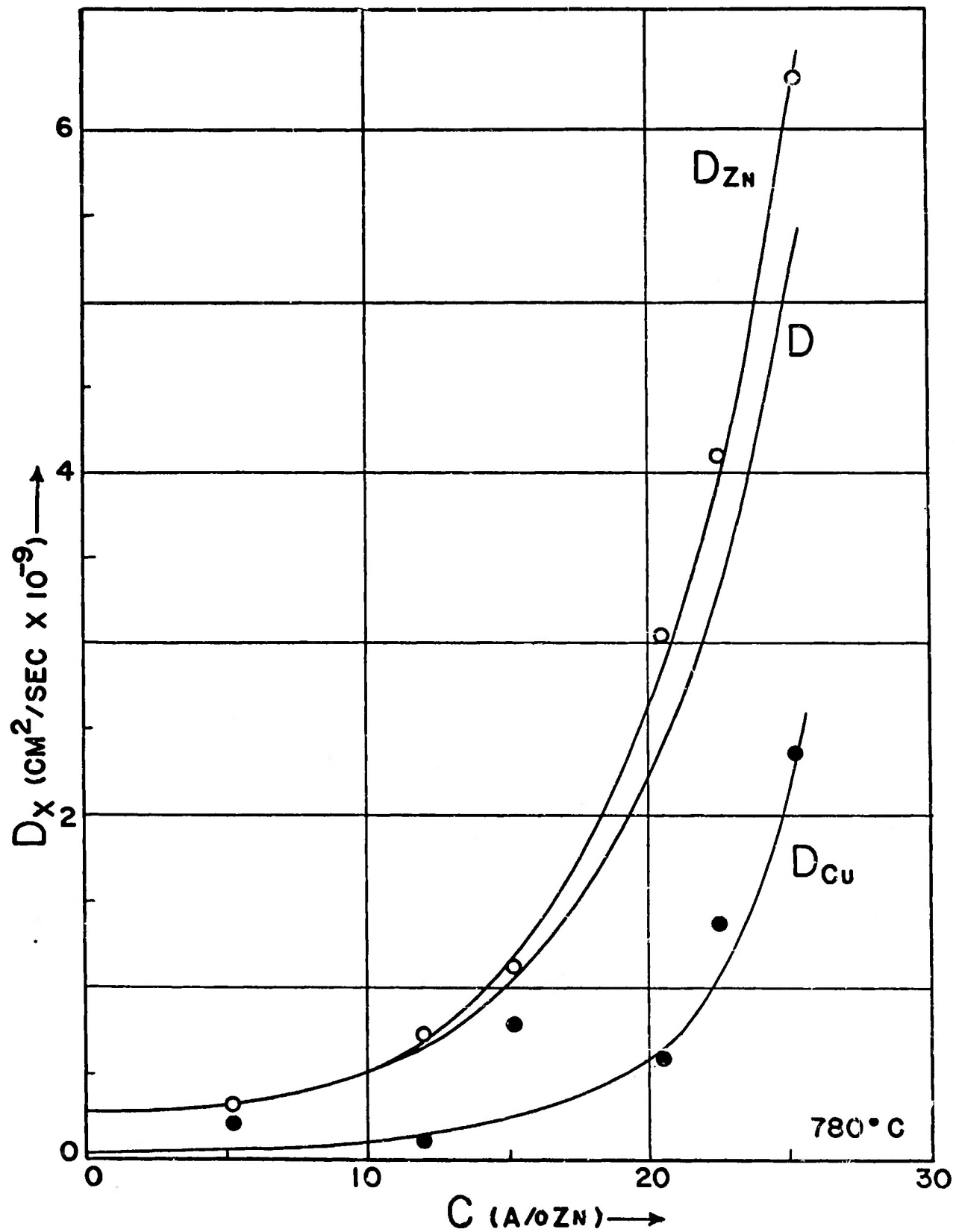


Fig. 17. General and individual diffusion coefficients vs concentration, 780°C.

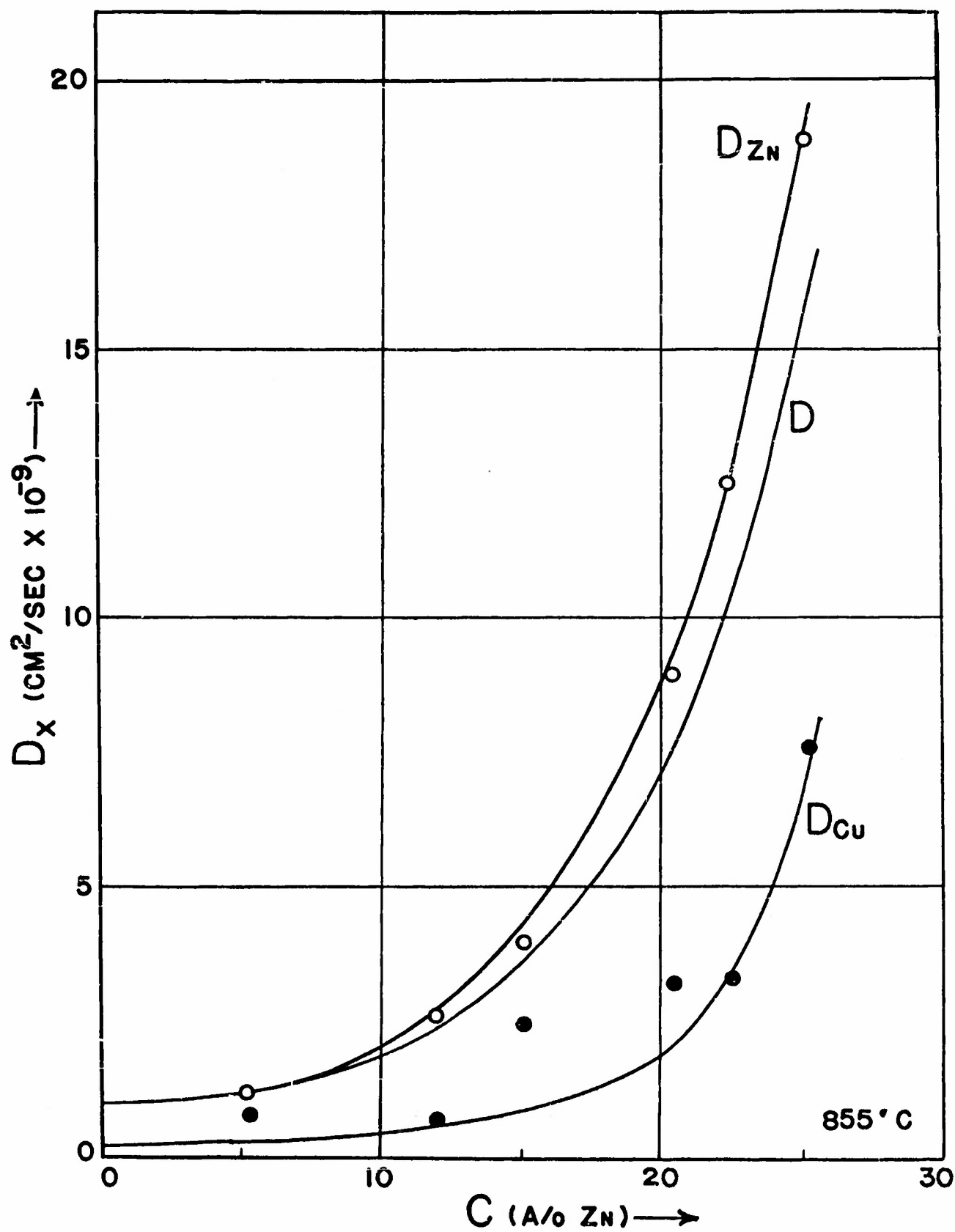


Fig. 18. General and individual diffusion coefficients vs concentration, 855°C.

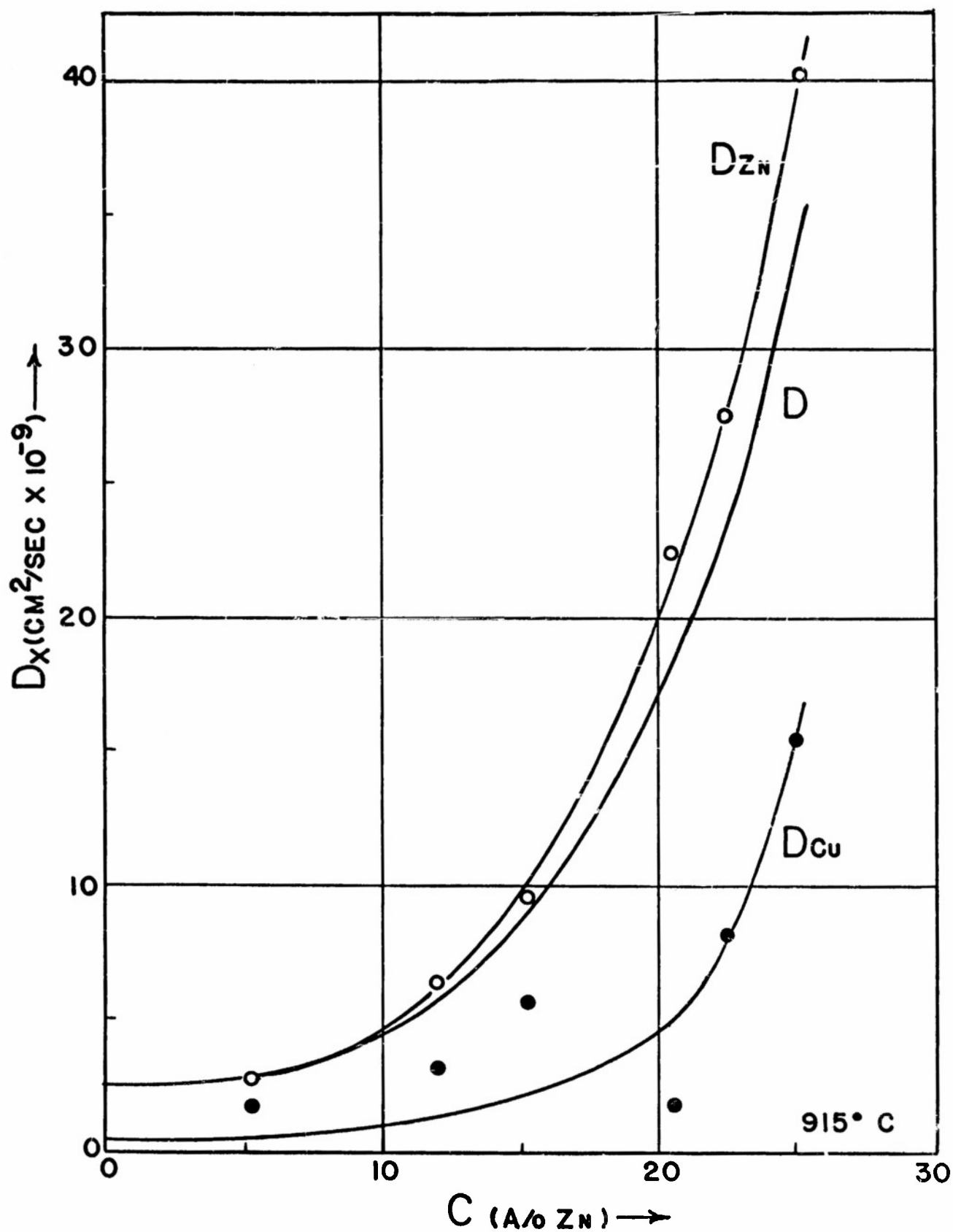


Fig. 19. General and individual diffusion coefficients vs concentration, 915°C.

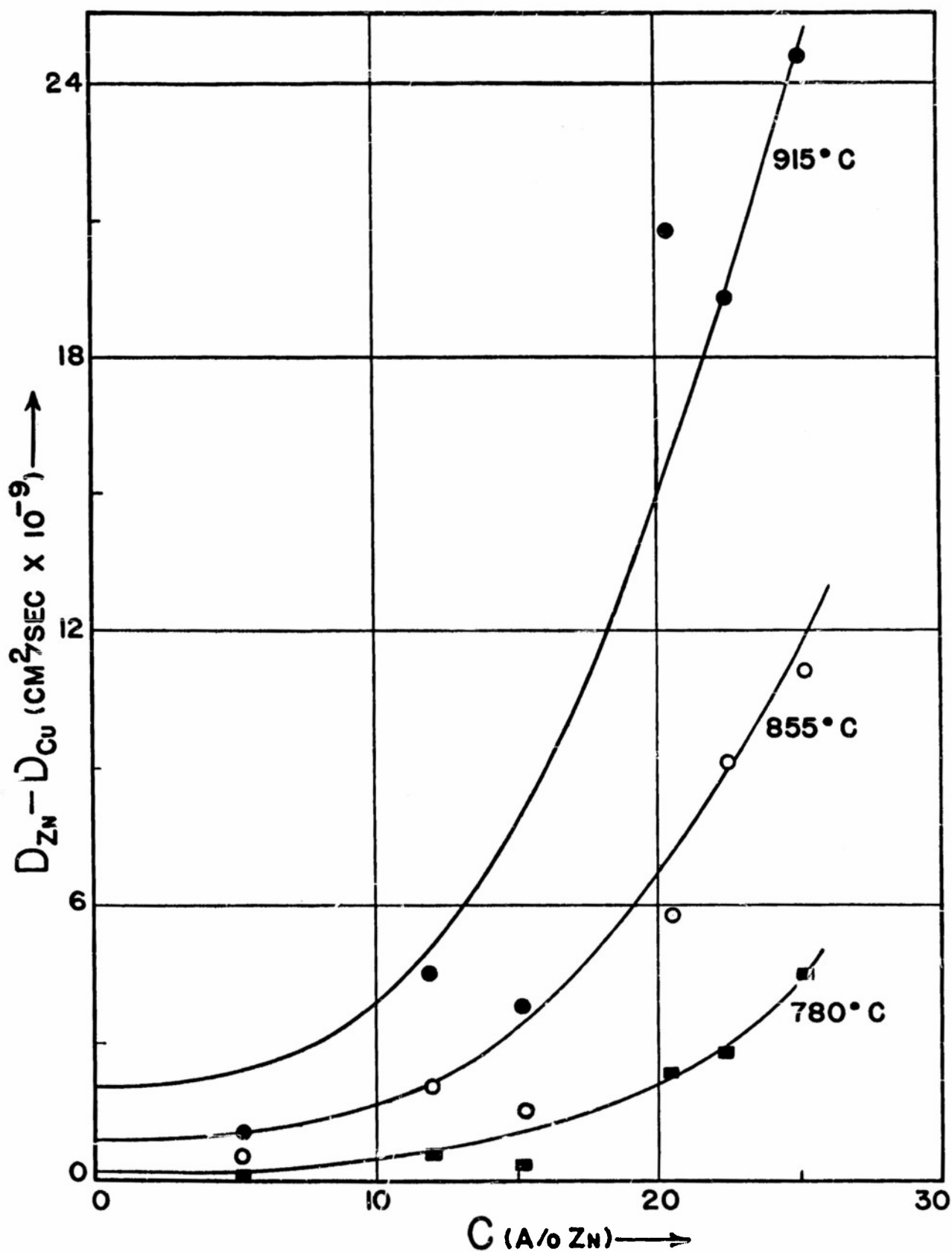


Fig. 20 The difference $D_{Zn} - D_{Cu}$ vs concentration.

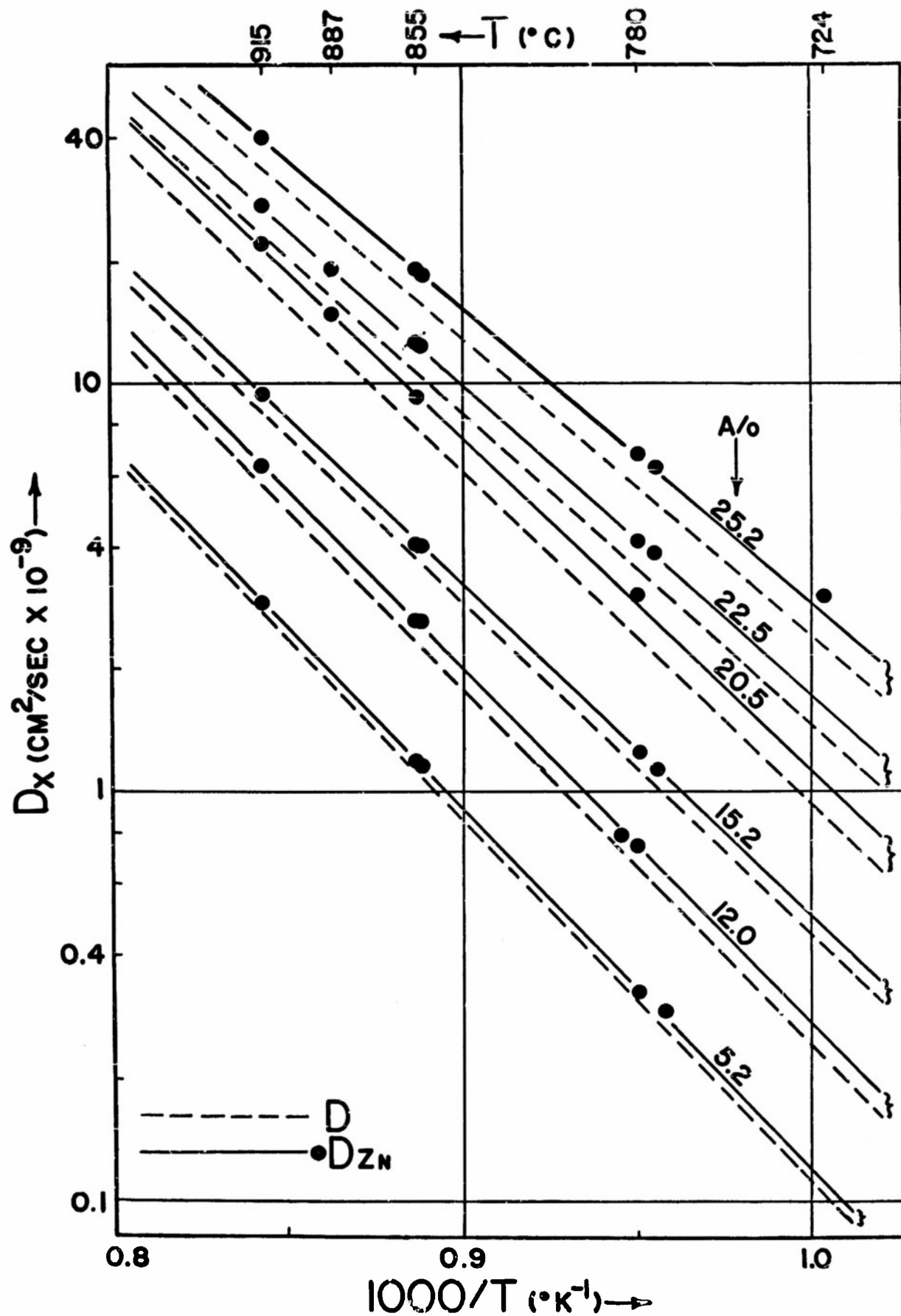
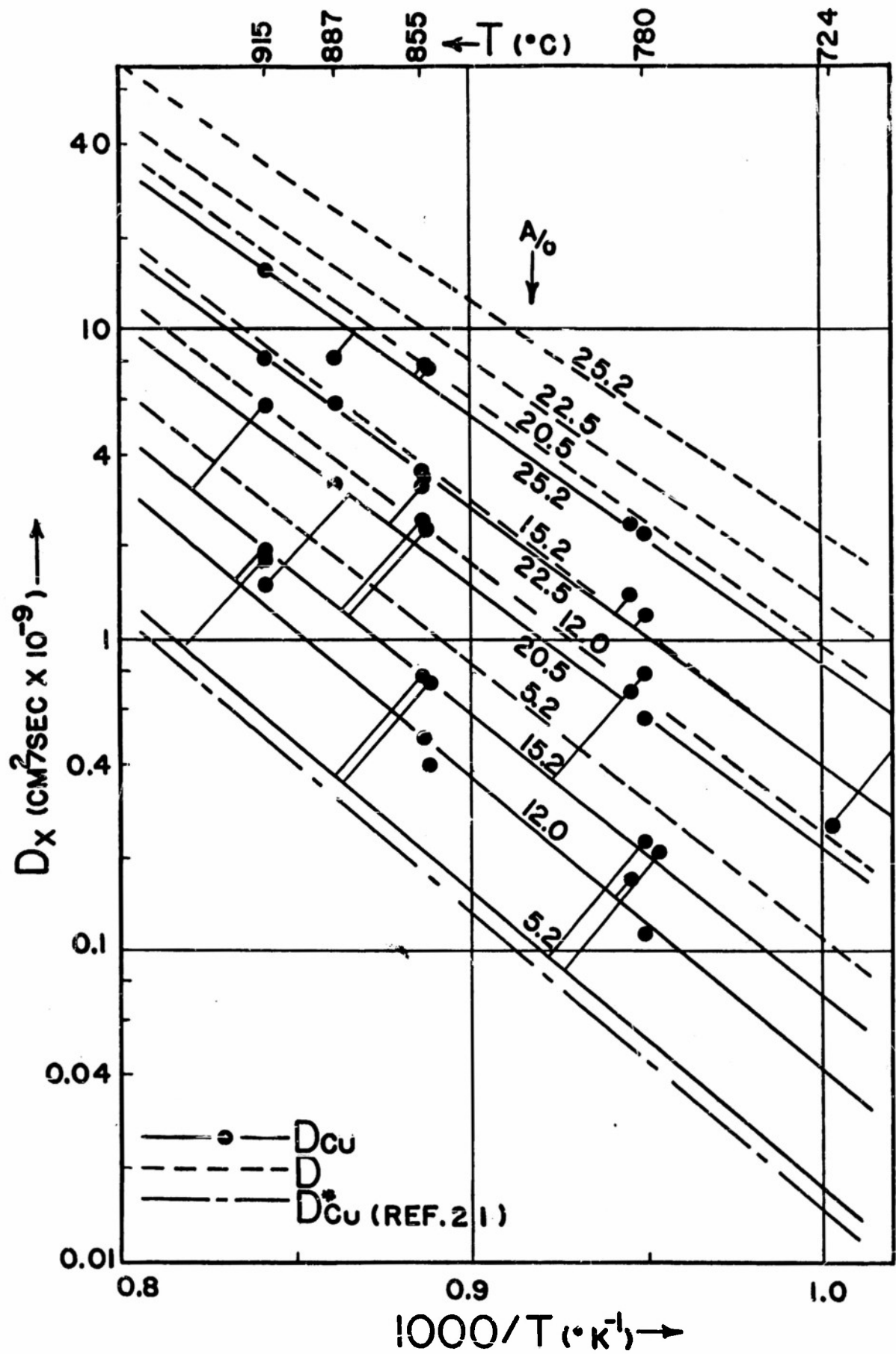


Fig. 21. Activation behavior vs concentration for D_{Zn} .

Fig. 22 Activation behavior vs concentration for D_{Cu}

the activation energy for D_{Zn} does not differ appreciably from that for D at the same concentration. On the other hand, the D_{Cu} values behave with some abandon. Since each of the individual diffusion coefficients depends on exactly the same four measured quantities, D , dN_{Zn}/dx , $v = x_m/2t$, N_{Zn} , much of the difference in behavior must be accounted illusory; because of the low fractional concentration of zinc, most of the difference $D_{Zn} - D_{Cu}$ appears as a difference between D and D_{Cu} , little between D and D_{Zn} ; the difference approaches D , leaving a very small 'residual' D_{Cu} ; and, between these two factors, a small error in $D_{Zn} - D_{Cu}$ becomes several hundred percent in D_{Cu} . Some smoothing of the data is obviously in order at this point.

The quantity D_{Zn} , being apparently little affected by experimental errors, was read directly from the activation plots as drawn; this is the 'smoothed' D_{Zn} . The difference $D_{Zn} - D_{Cu}$ was next corrected by drawing a smooth function $(D_{Zn} - D_{Cu})(c)$. Since we may expect that D_{Cu} will approach $D_{Cu}^*(0)$ (the self-diffusion coefficient of copper in pure copper) at low concentrations of zinc (otherwise the function $D_{Cu}(c)$ would be discontinuous), an attempt was made to extrapolate these functions through points representing $(D_{Zn} - D_{Cu}^*)(0)$ from the data of Maier and Nelson²¹ as the most recent. The extrapolation succeeded and the curves were drawn this way. This is, of course, the extrapolation attempted by Rhines and Mehl¹⁸, but in its proper form. The Rhines and Mehl extrapolation simply shows that the individual diffusion coefficients of several solutes in dilute solution in copper approach the same limiting value at zero concentration.

From the $(D_{Zn} - D_{Cu})(c)$ curves, it appears that some of the error is a more or less random error at a given concentration; in view of the scatter in D values obtained, this is to be expected. But there appears to be a systematic error also; it appears that the velocity of shift taken from the plots of shift vs. Matano area, must be in error in two cases. In the case of the 10/20 couples, where the difference is consistently low, the slope, shift vs Matano area, must be too low; depending as it does in this case on two couples (see Figure 13; an error in the direction of the deviation of couple 071 and in the center of couple 027 must be present here), this is somewhat surprising. In the 0/10 couples, where the difference is also low, the slope must again be too low; here the needed correction is less and almost within the remaining band of uncertainty (see Figure 14).

It is interesting to note that the curves were originally drawn in the manner indicated above; later a check was made to determine the curves which would follow if the 'least squares' line of Figure 15 were used, indicating a constant slope, shift vs. Matano area, independent of time, temperature or composition range within a given system (α Cu - Zn). The resulting values, D_{Zn} , D_{Cu} , $D_{Zn} - D_{Cu}$, are practically indistinguishable from the values obtained by the above 'smoothing' process. It is felt that this is good indirect evidence that the da Silva-Mehl relationship, marker shift is a linear function of the Matano area, is independent of time, temperature or concentration range in a given system. Furthermore, the above smoothing process explicitly assumes that the individual diffusion

coefficients, D_{Zn} , D_{Cu} , follow an activation behavior; an assumption, but not an unlikely one. Using the least squares' slope of Figure 14, however, activation behavior results and this is further evidence of the validity of the da Silva and Mehl relationship.

Calculation of the Individual Mobilities B_{Zn} , B_{Cu}

Darken's equations, solved for the individual mobilities in terms of the individual diffusion coefficients, D_{Zn} and D_{Cu} , the absolute temperature T , Boltzmann's constant k , the fractional concentrations N_{Zn} , N_{Cu} , and the activity coefficients

$$\gamma = \frac{a}{N} \text{ are}$$

$$B_{Zn} = D_{Zn} / \left[kT \left\{ 1 + N_{Zn} \left(\frac{d \ln \gamma_{Zn}}{d N_{Zn}} \right) \right\} \right]^*$$

$$B_{Cu} = D_{Cu} / \left[kT \left\{ 1 + N_{Cu} \left(\frac{d \ln \gamma_{Cu}}{d N_{Cu}} \right) \right\} \right]^*$$

The activity terms were evaluated from the data of Herbenar et al²²; these data differ little from those of Hargreaves²³ used by most investigators, but appear to be more self-consistent.

The resulting mobilities as a function of concentration are plotted in Figures 23-25 and an activation plot as Figure 26. Activation energies as calculated are shown in Table 12. The activation energies for the mobilities must follow the activation energies for the diffusion coefficients since the equality $D_{Zn}/D_{Cu} = B_{Zn}/B_{Cu}$ must be preserved.

* These equations reduce to the Einstein relation, $D = kTB$, in an ideal solution.

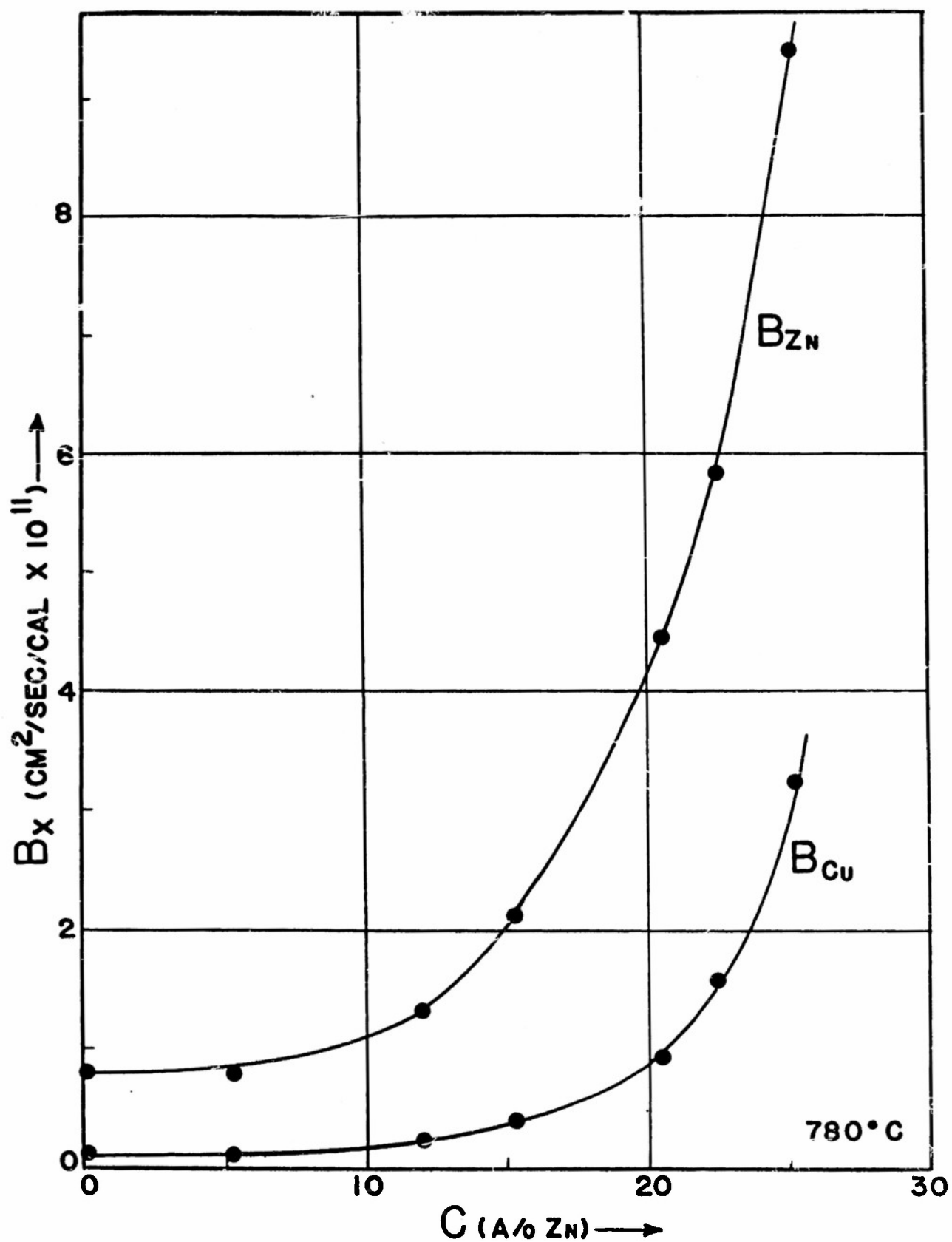


Fig. 23. The mobilities of zinc and copper vs concentration, 780°C .

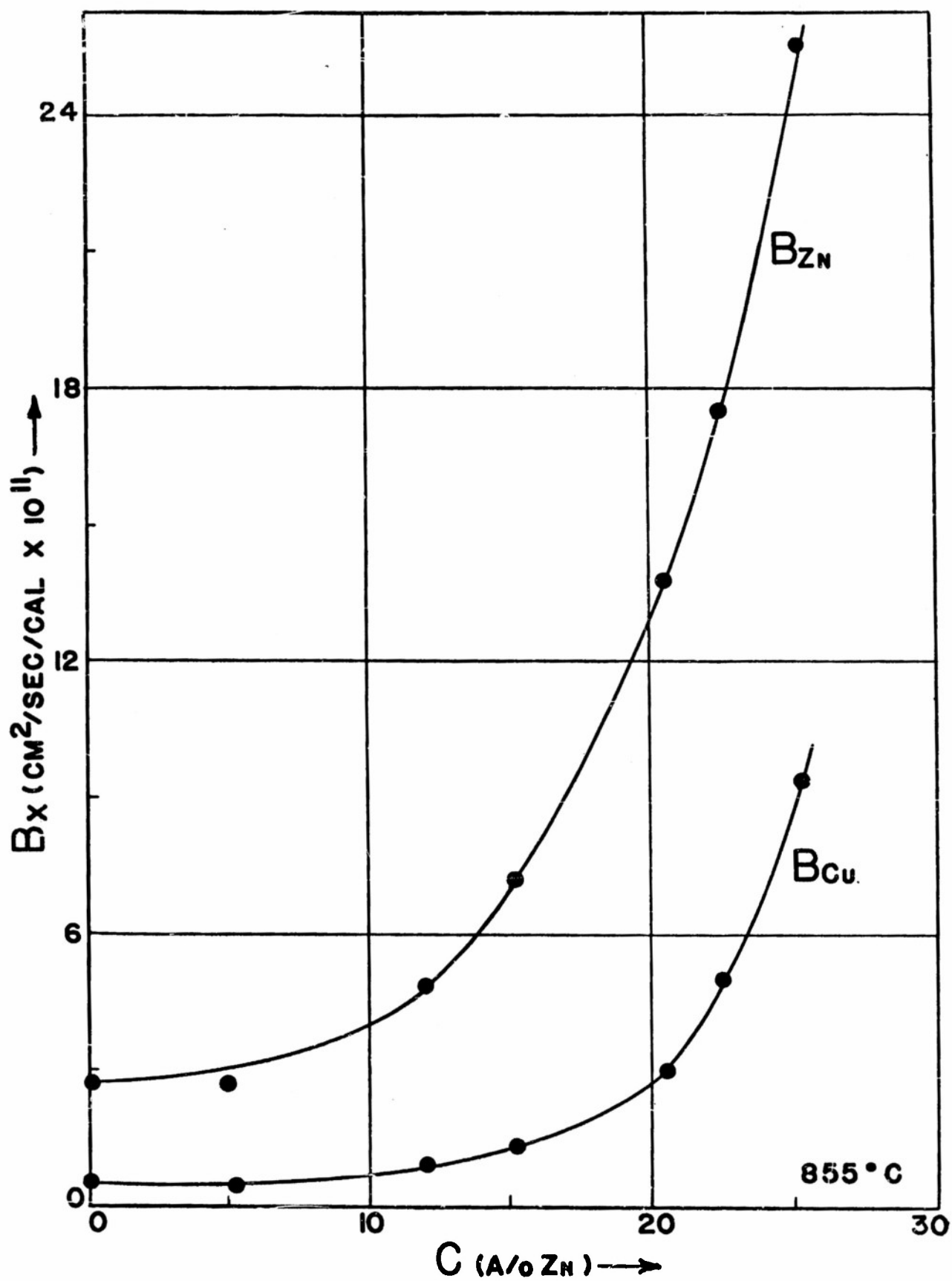


Fig. 24. The mobilities of zinc and copper vs concentration, 855°C .

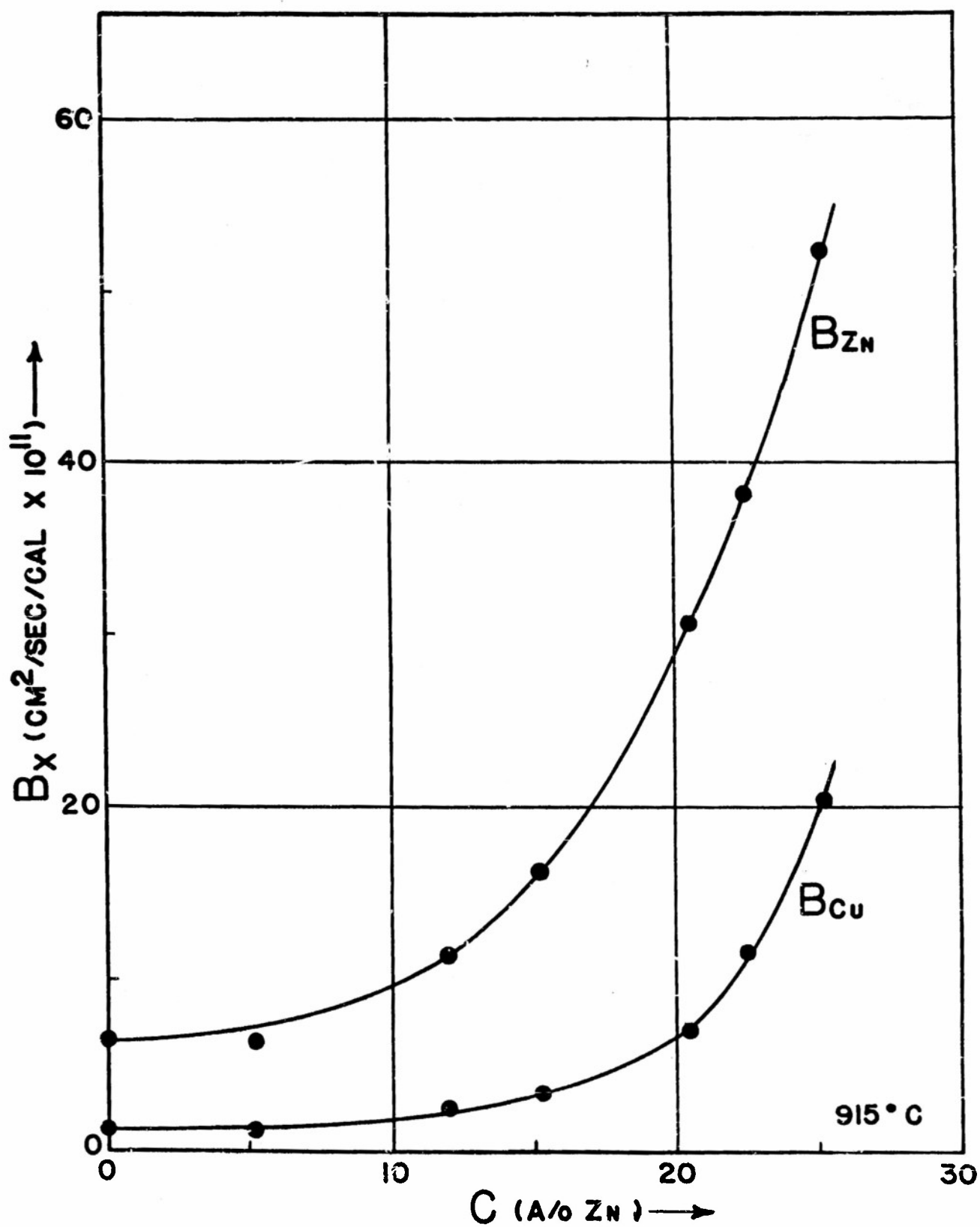


Fig. 25. The mobilities of zinc and copper vs concentration, 915°C .

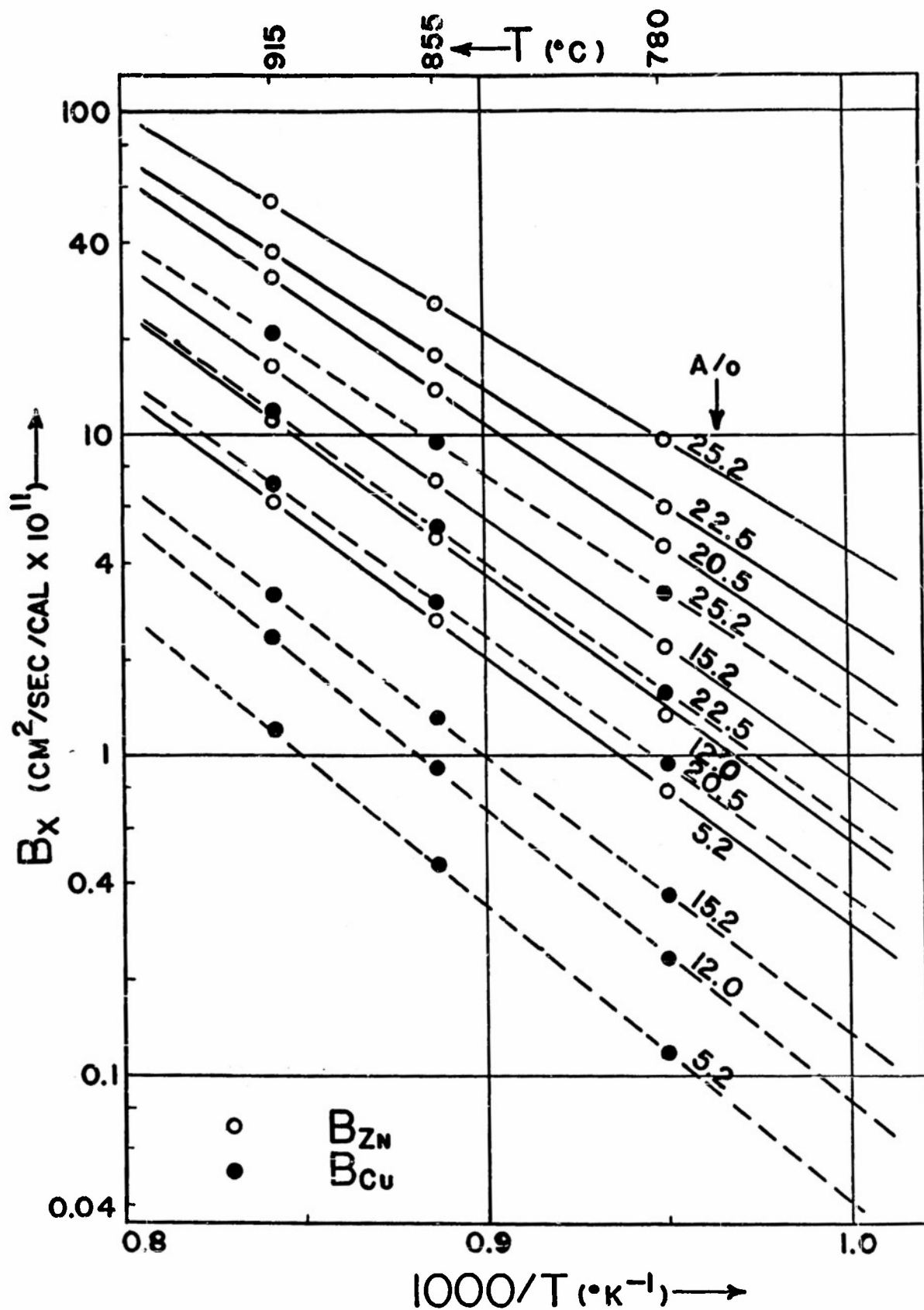


Fig. 26. Activation behavior vs concentration for mobilities of zinc and copper.

Table 12
Observed Activation Energies

Q(k cal)					
at A/o Zn	Q(D)	Q(D _{Zn})	Q(D _{Cu})	Q(B _{Zn})	Q(B _{Cu})
5.2	40	40	44.5	38	42
12.0	39	39	43	37.4	41.5
15.2	38	38	41	36.5	39.3
20.5	36.5	36.5	39	35.5	37.5
22.5	35.2	35.2	38	34	36.5
25.2	32.5	32.5	36	32.0	35.7

Theoretically, $Q(D_{Cu}) - Q(D_{Zn}) = Q(B_{Cu}) - Q(B_{Zn})$

DISCUSSION

The General Diffusion Coefficient, D

Experimentally, the general diffusion coefficient, D, has been determined as a function of concentration and temperature from incremental diffusion couples in the alpha-brass system. The results depend, except for experimental variables, only upon the Boltzmann-Matano solution to Fick's Law.

The Boltzmann-Matano solution to Fick's Law appears to yield results which are nowise as much in error as might be expected; it is a little surprising that the results obtained at the end of the concentration range of a given couple correspond so well to those near the center of another couple. In particular, there appears to be no grounds for assuming, as LeClaire¹⁶ has done, that determinations of D are suspect merely because a couple of large concentration range and the Boltzmann-Matano solution have been used; the results of Rhines and Mehl¹⁸, and da Silva and Mehl⁵ are closer to the present results, determined at least partly incrementally, than are those of Seith and Kraus¹⁷.

There appears, then, to be no evidence that the function $D(c)$ is not single-valued; the individual variation between couples is more than sufficient to account for previous equivocal results¹⁸. This variation is also sufficient to overshadow any second order corrections, such as could be made by a change to weight per unit volume from atomic percent.

No study of porosity in the reported couples was made and there are none in the literature known to the authors for other than 0/30 couples (in the alpha brasses); it can be assumed that the porosity would be less in any smaller range couple but the question of how much less is unanswered at the present time. But because of this and the apparent single-valuedness of D , as determined full range and incrementally, there is no discernible effect of porosity on the general diffusion coefficient.

The present values of $D(c,T)$ fall near the center of the range collected by Kubaschewski²⁴, but differ in that the present investigation found that the activation energy decreases with increasing zinc content; the same result was found, to an even greater degree, by da Silva and Mehl⁵. From investigations of this type, with or without the low temperature determinations based on anelastic phenomena, little reliance can be placed on the D_0 values. Similarly the absolute accuracy of the values of D is indeterminate depending, as it does, on so many operations, particularly manual.

The Individual Diffusion Coefficients, D_{Zn} , D_{Cu}

Experimentally the magnitude of the Kirkendall effect has been determined for six types of diffusion couples within the alpha brass range; these results have been used, through Darken's analysis, to yield values of the individual diffusion coefficients, D_{Zn} and D_{Cu} . These values depend on experimental variables, on Darken's analysis and on two experimental relations reported by da Silva and Mehl.

The coincidence of the Matano interface and the original weld interface, experimentally observed by da Silva and Mehl, has been used to position the original interface in the couples studied here. The linear relation between the shift of a marker and the Matano area in a given type of couple, also observed by da Silva and Mehl, has been used to remove experimental uncertainties in the amount of shift. These have been accepted as experimental facts, valid within the limit of accuracy of the techniques; the reader is referred to the original paper⁵ for a discussion of these; nothing in the present data appears to be at variance with their findings.

There are unresolved doubts as to the assumptions implicit in Darken's analysis²⁵, but, again, there does not appear to be any aspect of the present data which in itself casts doubt on the analysis.

The presence of porosity affects the calculation of the marker shift when the shift is determined in the present fashion. Again, there are no available data to attempt to correct all shifts for this factor; even in O/30 couples there is some uncertainty as to the magnitude of the correction and the manner of its proper application, and little information on variation

with temperature. The expected influence would be to increase the variation of D_{Zn} and E_{Zn} with concentration. But it is felt that the accuracy inherent in the technique does not justify all such corrections even though they were available.

There is one disturbing feature present. Once again scatter was observed in the concentrations at the wire interface; they varied by 0.5 A/o Zn in some cases. There is no evidence that this varying concentration at the wire (C_w) is a function of temperature; it is on occasion the same at high temperatures as at low but different at intermediate temperatures; the concentration at the Matano interface shows similar behavior. There is no evidence that this varying C_w is a function of time; the variation with time at a given temperature and type of couple appears to be less than the general scatter. Yet, for a 0/30 couple, Smigelskas and Kirkendall⁴ found the wires marking about 22.0 A/o Zn; da Silva and Mehl⁵ found values scattered around 21.3 A/o Zn (they thought they detected a variation with temperature; Thomas and Birchenall¹⁹ dispute this in the Cu-Ni system); the wires were found in the present 0/30 couples scattered around 20.5 A/o Zn. In the penetration curves obtained by the present authors, the distance between 20.5 A/o Zn and 22.0 A/o Zn at 780°C (Smigelskas and Kirkendall worked at 785°C) and 400 hours elapsed time was about 200×10^{-4} cm, some 200 percent greater than the observed shift, the rate of which agrees with that of Smigelskas and Kirkendall within 12 percent. All that the present authors can say is that there is no apparent reason why the large difference in concentration at the markers is observed.

SUMMARY AND CONCLUSIONS

1. The general diffusion coefficient, D , and the individual diffusion coefficients D_{Zn} and D_{Cu} have been measured in alpha brass as functions of concentration and temperature using Darken's analysis on data from incremental diffusion couples of overlapping range. The basic data were obtained directly from concentration-penetration curves using the Matano interface as the original interface.
2. Experimentally, the coefficient relating marker shift to Matano area is a constant independent of time, temperature and the concentration range of the diffusion couple in the above system.
3. Using the above diffusion coefficients and activity data from the literature, mobilities of zinc and copper were determined as functions of concentration and temperature.
4. The diffusion coefficients and mobilities are single-valued functions of the concentration to within the limits of the experimental method.
5. As expected, neither the individual diffusion coefficients nor the mobilities are simple functions of the concentration; they are all of the same form as the usual D vs c curve.
6. The individual diffusion coefficient D_{Cu} approaches the self-diffusion coefficient for copper, D_{Cu}^* (o), at low concentrations of zinc.
7. Discrepancies were observed as to the concentration at which a marker is found; no solution was suggested.

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